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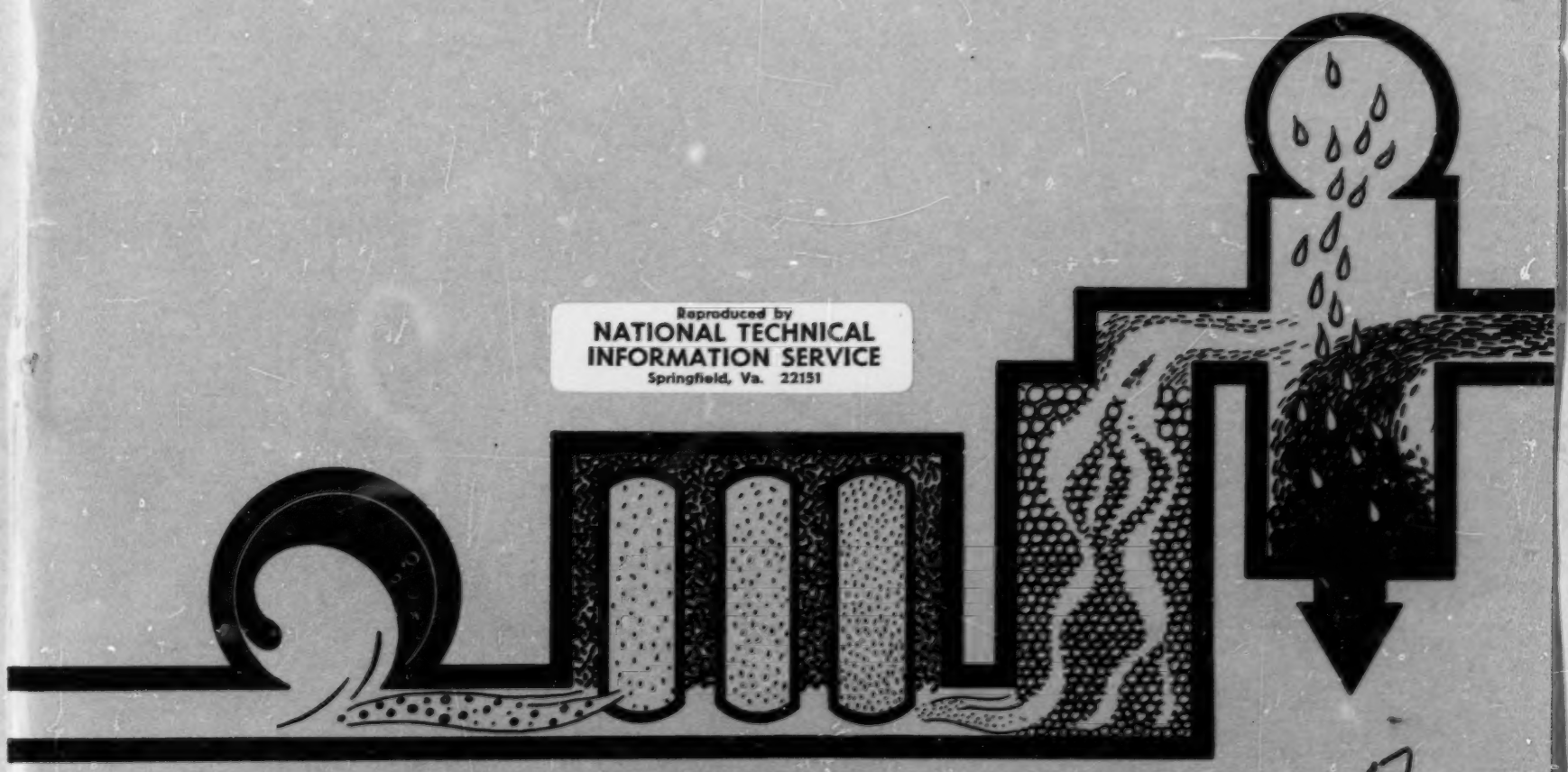
THE ELECTRO-OXIDATION OF AMMONIA IN SEWAGE TO NITROGEN



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16. Abstract Laboratory tests were conducted to determine the feasibility of electro-oxidation as a means of removal of ammonia from wastewaters. It was determined that, under conditions of ammonia concentration and pH typical of treatment effluents, the electro-oxidation reaction proceeded stoichiometrically to nitrogen and no other oxidation products. Oxidation occurred in concentrations as low as 2 mg/l of ammonia. Using platinized platinum as an electrode, ammonia decomposition occurred in a narrow potential range with high coulombic efficiency, assuming a three-electron exchange per ammonia molecule. Conversion of nitrogen to the elemental form was demonstrated by analysis of the gas from the anode. No detectable quantities of nitrite, nitrate hydrazine, and hydroxylamine were discovered in the gas. Electric power costs were estimated at $.01/1000 gallons, but cost of the platinum electrodes was prohibitive. Experiments with other electrodes were unsuccessful. Unless less expensive electrodes are developed, the process cannot be economically competetive with other methods. (Lowry-Texas)

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THE ELECTRO-OXIDATION OF AMMONIA IN SEWAGE TO NITROGEN

by

Ionics, Incorporated
Watertown, Massachusetts 02172

for the

WATER QUALITY OFFICE

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ABSTRACT

A study was undertaken to determine the feasibility of electro-oxidation of ammonia as a possible new method for ammonia removal during sewage treatment. Initial tests were conducted with platinized platinum and showed that ammonia decomposition occurred in a narrow potential range with high coulombic efficiency, assuming a three-electron exchange per ammonia molecule. Conversion of nitrogen to the elemental form was shown by analysis of the gas from the anode. Analysis of the electrolyzed water for nitrite, nitrate, hydrazine, and hydroxylamine indicated these materials were not formed in measurable quantities. Their absence suggests a high degree of conversion of ammonia nitrogen to the elemental form.

Following the initial determination of technical feasibility, a survey was made of electrodes having lower cost than platinized platinum. Only electrodes containing a significant amount of platinum were found capable of converting ammonia nitrogen to elemental nitrogen. The cost of these electrodes is too high to make this ammonia removal method competitive with other existing methods. A cheaper electrode that can operate at significantly higher current densities is needed to bring the cost in line with the cost of these other methods.

This report was submitted in fulfillment of Project Number 17010 EED, Contract 14-12-800, under the sponsorship of the Water Quality Office, Environmental Protection Agency.

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INTRODUCTION

Ammonia in wastewater has two detrimental effects upon receiving waters. Because it is a plant nutrient, it encourages excessive algal growth. Because of its conversion to nitrate in the receiving waters, it exerts a very significant oxygen demand. As a result of these undesirable characteristics there is an increasing need for ammonia removal from wastewaters. Air stripping at high pH, bio-oxidation to nitrate, selective ion exchange, and breakpoint chlorination are existing methods for accomplishing this removal, but none of these methods is entirely satisfactory. There is need for an effective and inexpensive ammonia removal technique.

A very desirable property of an ammonia removal method is the ability to convert the nitrogen in the ammonia to elemental nitrogen which causes no further pollution of the environment. Studies concerned with ammonia in fuel cells indicated that electrooxidation of the ammonia had a good potential for producing elemental nitrogen. This fact, and the knowledge that power requirements for applying this treatment method to domestic wastewater should be very low, led to the present feasibility study.

THEORY

Recent years have seen the development of substantial interest in ammonia as a possible fuel-cell reactant because of its high content of hydrogen. That interest has raised the question of the electrochemical behavior of ammonia, i.e., of the mechanism and kinetics of its reactions at anode surfaces. Several papers dealing with this problem have appeared (1-4) with contradictory results in regard to kinetics (2,4) but with general agreement that the overall electrochemical reaction at the spontaneously established negative potential is a three-electron exchange reaction yielding nitrogen and water as products with almost 100% faradaic efficiency:

$$NH_3 + 3OH^- \rightarrow 1/2\ N_2 + 3\ H_2O + 3e^- \qquad [1]$$

A platinized platinum anode, a highly active electrocatalyst, was used in experimental work by all of these authors. T. Katan et al (1) found that current efficiency of reaction [1] using platinum black as the anode was 99.7% at current densities (c.d.)$\leq$ 100 mA/cm^2 and anode potentials of -0.31 to +0.15V.

All of the experiments were conducted in strongly alkaline solutions (in the range of 0.1 - 6.9N KOH) and ammonia concentrations ranging from 0.03M to 6M. H.G.Oswin et al (2) suggested that oxides of nitrogen would be expected only at potentials positive to a standard hydrogen electrode. All of his experiments were conducted in the potential region negative to SHE where visible gas evolution was observed. The gas was identified as pure nitrogen. He too stated that overall reaction [1] proceeds with 100% coulombic efficiency.

Anodes of smooth platinum and other metals were tried (3,5,6) but nitrogen was never produced in quantities which corresponded to complete stoichiometric reaction of ammonia as indicated by Eq.[1] . Instead substantial quantities of nitrate and lesser quantities of nitrite ions were formed:

$$NH_3 + 7OH^- \rightarrow NO_2^- + 5H_2O + 6e^- \qquad [2]$$

$$NH_3 + 9OH^- \rightarrow NO_3^- + 6H_2O + 8e^- \qquad [3]$$

Various workers (2,3,4), studying the electrochemical kinetics of the ammonia oxidation reaction in alkaline solutions on platinum black surfaces, reported the proposed kinetic scheme of consecutive

reactions, theoretical current-voltage relationships for various rate-determining mechanisms, and experimental current-voltage relationships. There are four sequential steps in the proposed anodic oxidation of ammonia. In these equations the electrode surface is represented by M.

$$NH_3 + M + OH^- \rightarrow M\text{-}NH_2 + H_2O + e^- \qquad [4]$$

$$M\text{-}NH_2 + OH^- \rightarrow M{=}NH + H_2O + e^- \qquad [5]$$

$$M{=}NH + OH^- \rightarrow M{\equiv}N + H_2O + e^- \qquad [6]$$

$$M{\equiv}N + M{\equiv}N \rightarrow 2M + N_2 \qquad [7]$$

The electrode surface would be then covered with $-NH_2$, -NH, and -N species. Most of the authors agreed that step [5] is the rate-determining step in the process of the anodic oxidation of ammonia.

EXPERIMENTAL

Procedures

Potentiodynamic procedures have been employed in most of this work using a Heath Polarography System Model EUW-401.* This system consists of Polarography Module EUA-19-2, operational Amplifier System Model EUW-19A, operational Amplifier Chopper Stabilizer Model EUA-19-4 and Servo Recorder Model EU-20B. The polarography module includes the potentiostat, initial potential source, linear potential sweep generator and current measuring amplifier. In some experiments, the steady-state potentiostatic procedure was also used, current-potential relationships being determined point by point (20 mV steps) at controlled intervals of time (1 minute). All potentials are referred to the standard hydrogen electrode (SHE) and are designated E_H .

Electrochemical Cells

All-glass electrochemical cells of conventional design (Figure 1) were used for most of this work. The central compartment contained the working electrode and had a sufficient volume to minimize concentration changes during the experiments. The platinized platinum gauze counter electrode was in a compartment separated from the main compartment by a fritted glass. The reference electrode was mercury/mercuric oxide in 1M KOH. In some experiments a saturated calomel electrode was used.

In the first part of the experimental work, the working electrode was a platinized platinum electrode (bulb-type rotating electrode after Laitinen-Kolthoff) rotated by a Sargent Constant Speed Stirring Motor (600 rpm). A standard electrode cleaning treatment (7) was used prior to platinization. The platinizing procedure from the same source (7) yielded black deposits. The same procedure was used before each set of measurements. Geometric area of the electrode was 0.13 cm^2 .

Experiments were conducted at room temperature in various supporting electrolytes (NaCl, K_2SO_4, KOH, phosphate buffer and K_2HPO_4) with pH values varying from 5.55 to 12.8 and ammonia concentrations from 0.00012M to 0.01M (~ 2 to 170 mg/l).

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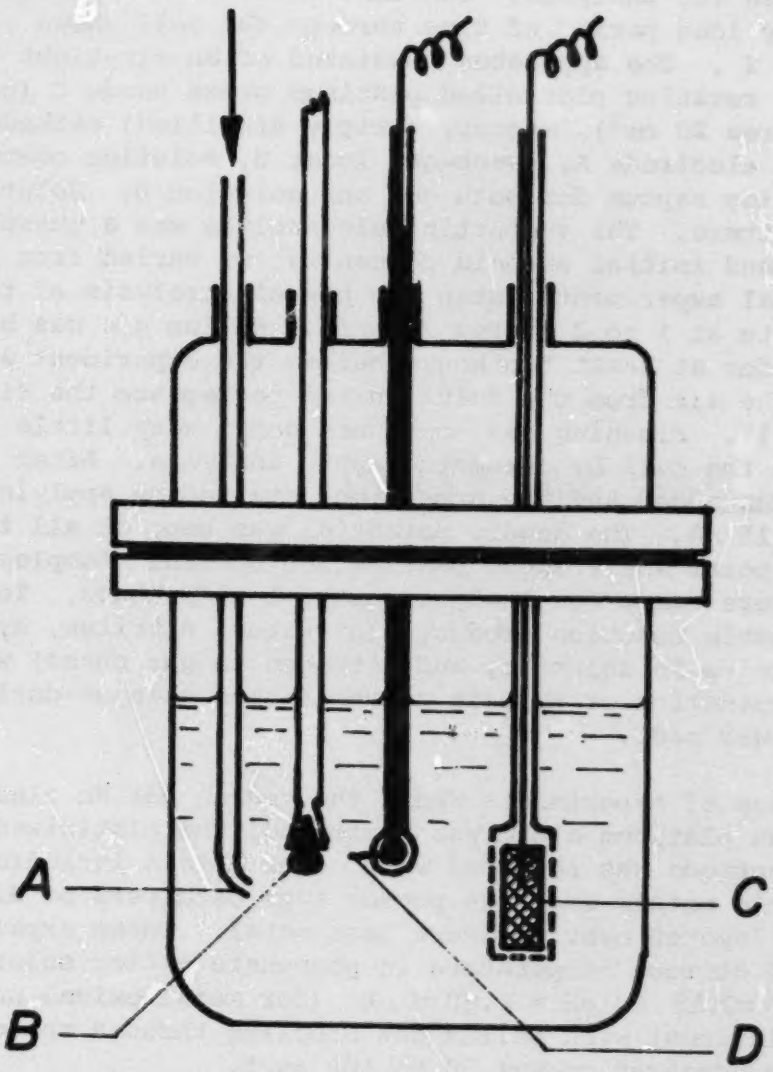


A - gas inlet

B - ref. electrode

C - counter electrode

D - working electrode

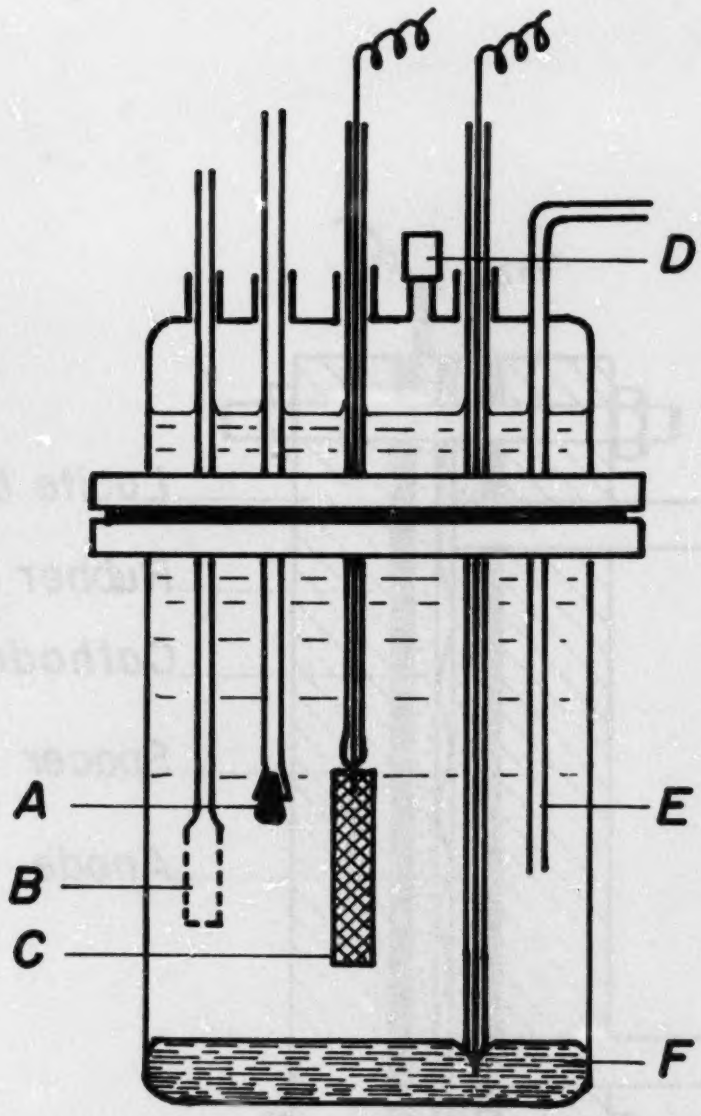
Figure 1. Experimental Cell for Investigating Anodic Oxidation of Ammonia

To determine the course of the reaction, experiments were continued with a larger platinized platinum electrode and reaction products accumulated for analysis. Constant current was applied for a comparatively long period of time through the cell shown schematically in Figure 2 . The apparatus consisted of an air-tight Pyrex glass cell with rotating platinized platinum gauze anode C (geometrical surface area 20 cm^2), mercury (triply distilled) cathode F, Hg/HgO reference electrode A, sweep-gas inlet B, solution overflow outlet E, and sampling septum for both gas and solution D. Solution content was 1.2 liters. The supporting electrolyte was a phosphate buffer (pH 8.2) and initial ammonia concentration varied from 40 to 55 mg/l. The initial experimental step was pre-electrolysis of the supporting electrolyte at 1 to 2 mA for 2 hours. Helium gas was bubbled through the cell for at least two hours before the experiment was started to exclude the air from the solution and to replace the air at the top of the cell. Flushing was continued until very little air was detected in the cell by chromatographic analysis. After flushing, the ammonia was added and the experiment started by applying a current of 10 to 15 mA. The anodic potential was kept at all times below the critical point where anode passivation occurs. Samples of solution and gas were taken for analysis every 1 to 2 hours. Tests for the most probable reaction products (nitrates, nitrites, hydrazine and hydroxylamine in solution, and nitrogen in gas phase) were performed and determination of ammonia concentration changes during the oxidation reaction was made.

In a series of experiments where the search for an electrocatalyst other than platinum alone was performed, the platinized platinum micro-electrode was replaced with other metals including bright or black noble metals and with powder type catalysts of different composition layered over an inert base metal. These experiments were conducted at room temperature in phosphate buffer solution of $pH = 8.00 \pm 0.15$ or $pH = 6.60 \pm 0.05$ (for metal oxides unstable in basic solutions) with helium gas bubbling through the cell. The ammonia concentration was 50 to 100 mg/l.

A continuous flow electrolytic cell was used to simulate one of many parallel channels in a full size prototype. The cell, shown schematically in Figure 3, contained a platinized titanium anode and a stainless steel cathode with the cell volume and active electrode surface defined by a polyethylene spacer between the electrodes. A top view and a cross-section of the spacer is shown in Figure 4. The active electrode area in the cell was 60 cm^2 with a flow path length of 90 cm and a path width of 0.7 cm. No membrane or diaphragm was used to separate the electrodes. A test solution was prepared from ammonia and a pH buffer at values typical of wastewater effluents (about 30 mg/l ammonia, pH 8).

The experimental set up included a feed solution reservoir containing 13 liters of test solution. The solution was fed to the cell by a



A- ref. electrode
B- gas inlet
C- anode
D- sampling outlet
E- overflow
F- cathode

Figure 2. Experimental Cell for Determination of Ammonia Oxidation Reaction Products

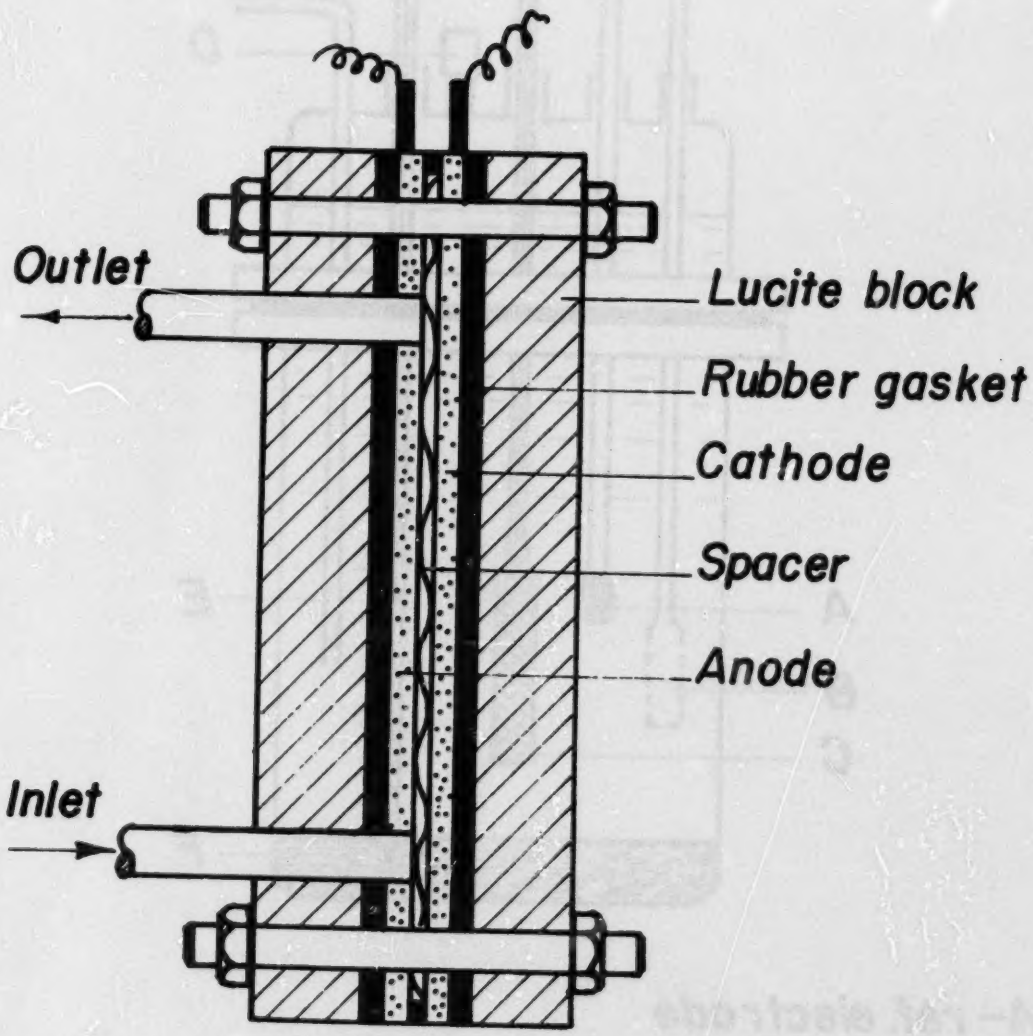


Figure 3. Continuous Flow Bench Scale Electrolytic Cell

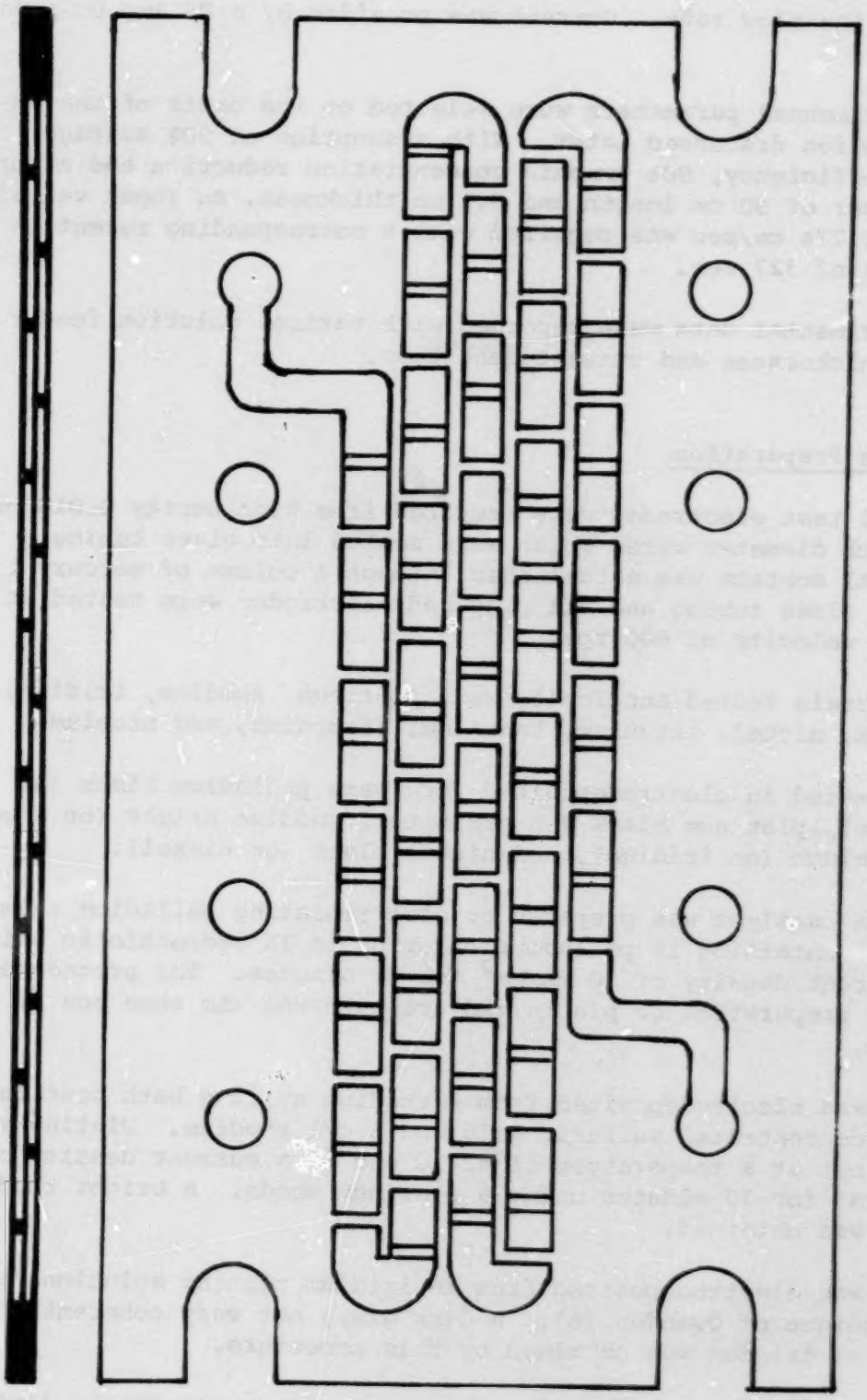


Figure 4. Top View and Cross-section of the Tortuous Path Spacer

centrifugal pump. A rotameter, calibrated by effluent collection, measured the flow rate. Current was provided by a 25 amp DC power supply.

The experimental parameters were selected on the basis of the design equation discussed later. With assumption of 50% average current efficiency, 90% ammonia concentration reduction and a tortuous path spacer of 90 cm length and 0.1 cm thickness, an input velocity (V_o) of 0.274 cm/sec was required with a corresponding retention time (t_R) of 327 sec.

The experimental data were recorded with various solution feed rates, spacer thicknesses and current densities.

Electrode Preparation

The small test electrodes were prepared from high purity 0.010 or 0.020 inch diameter wires which were sealed into glass tubing. Electrical contact was established through a column of mercury inside the glass tubing and all prepared electrodes were tested at a rotating velocity of 600 rpm.

Smooth metals tested anodically were platinum, rhodium, iridium, palladium, nickel, titanium, tantalum, zirconium, and niobium.

Metals tested in electrodeposited form were palladium black (on palladium), platinum black (on graphite), rhodium bright (on rhodium), iridium black (on iridium), and nickel black (on nickel).

Palladium catalyst was prepared by electroplating palladium from a solution containing 1% palladous chloride in 1N hydrochloric acid at a current density of 30 mA/cm^2 for 30 minutes. The procedure used for preparation of platinized graphite was the same one as for platinum.

Rhodium was electrodeposited from a rhodium sulfate bath containing 20 ml/l concentrated sulfuric acid and 2 g/l rhodium. Plating was carried out at a temperature of 42° C and at a current density of 100 mA/cm^2 for 30 minutes using a platinum anode. A bright rhodium deposit was obtained.

Iridium was electrodeposited from an iridium plating solution using the technique of Ovenden (8). A dark grey, not very coherent, deposit of iridium was obtained by this procedure.

A nickel catalyst was prepared in the form of a very finely divided black deposit by electrodepositing nickel from a bath containing 33 g/l of nickel ammonium sulfate and 14 g/l of Rochelle salt at a current density of 100 mA/cm^2, at 20°C, and at a pH of 6.6 .

Manganese dioxide was deposited by anodic electrodeposition at 80°C and at a current density of 2 mA/cm^2 from a bath containing 50 g/l anhydrous $MnSO_4$ and 65 g/l H_2SO_4. Deposition time was 25 minutes.

The electrodes for testing electrocatalysts in a powdered form were prepared by coating 0.02 inch diameter titanium wire, titanium coupons, or expanded titanium (9 mil overall thickness with mesh dimensions of 0.055 in. x 0.0285 in. and approximately 700 openings per square inch) with a mixture of powdered catalyst and Teflon T-30 dispersion as binder.

Teflon T-30 is an aqueous dispersion of Tetrafluoroethylene (TFE) resin particles containing about 60% solids, the rest being water and "Triton X-100" stabilizer (a non-ionic wetting agent). Special heat treatment is required in order to remove water and stabilizer, which decomposes cleanly at temperatures between 250 and 300°C, leaving a contaminant-free polymer.

Two coating procedures were tested. Coating procedure #1 was as follows:

- Mix conducting material throughout T-30 dispersion by very slow agitation (rapid agitation causes irreversible coagulation).
- Dip titanium support into dispersion for even layering. If too much pick-up occurs per dip, dilute mixture with water.
- Place coated electrodes in furnace, which is gradually heated from room temperature to 250°C. Water is removed by this procedure from the coated catalyst mixture.
- Heat for 3 hours at temperatures between 250 and 300°C to remove stabilizer.
- Sinter for 4 to 5 minutes at 360°C (melting point of TFE resin).
- For further applications of the catalytic mixture, cool electrodes rapidly, apply next coating and repeat heating procedure. After last application cool the electrodes slowly to provide even annealing which is needed for good adhesion.

Technique #2 includes two steps:

- Dry the applied mixture for 5 to 10 minutes under an infrared lamp.
- Bake and sinter at 320°C and 1500 to 2000 psi.

The desired pressure and temperature were provided by a hydraulic press with heated platens. Pretreatment of the titanium support consisted of cleaning in hot (70°C to boiling) hydrochloric acid (8 to 12N) for 5 to 15 minutes. Graphite and tungsten bronzes were often used in mixture with the catalyst to improve the electrical conductivity and to dilute the expensive catalyst. It has been shown that, by incorporation of tungsten bronzes into the platinum black anodes, the electro-oxidation of carbon monoxide and reformer gas can be appreciably enhanced(9). The attempt was made to use the platinum catalyst more effectively in the ammonia oxidation reaction by addition of tungsten bronzes to the catalyst in different ratios.

Sodium tungsten bronzes with the general formula Na_xWO_3 and high sodium content were prepared according to a modified Straumanis (10) procedure.

Platinum electrodeposition on titanium and tantalum was carried out using the same procedure as for platinizing platinum. Tantalum electrodes were treated prior to platinization cathodically applying 100 mA/cm^2 for 15 minutes in 2% sulfuric acid solution. Titanium was pretreated in hot hydrochloric acid the same way as for powder-catalyst electrode preparation.

Analytical Techniques

A Hach DC-DR photoelectric colorimeter was used for liquid phase analysis. The ammonia nitrogen was determined by Nessler's method with a minimum detectable nitrogen concentration of 0.05 mg/l.

The cadmium reduction method which is a modified diazotization (1-naphthylamine-sulfanilic acid) method was employed for the nitrate nitrogen determination. Minimum detectable nitrate nitrogen concentration was 0.1 mg/l .

For determination of nitrite nitrogen a diazotization method (1-naphthylamine-sulfanilic acid) was used with minimum detectable nitrite nitrogen concentrations of 0.01 mg/l. Hydrazine tests were performed using the 4-dimethylaminobenzaldehyde method. The method is very sensitive and is used for determination of small amounts of hydrazine. Minimum detectable concentration was 0.01 mg/l.

The hydroxylamine test was based on the reaction with benzoyl chloride and ferric chloride and the method was modified for colorimetric analysis in low concentrations.

Chromatographic analysis of the gaseous phase was conducted using an Aerograph Gas Chromatograph Model A-90-P3.

RESULTS AND DISCUSSION

Platinized Platinum Micro-Electrode

The first set of experiments was conducted in alkaline solutions (pH 12.8 to 13.0) with KOH as the supporting electrolyte and ammonia concentrations varying from approximately 0.001M to 0.003M (17-51 mg/l). Potentiodynamic and potentiostatic techniques were employed. Single potential sweep current-potential curves recorded with stationary and rotating platinized platinum micro-electrodes in the same solution are shown in Figure 5. An anodic current peak which appears at -0.1 V with the stationary electrode was slightly shifted towards more positive potentials (0.05 to 0.25 V) and increased in height about five times when the rotating electrode was used. Current maxima for stationary and rotating platinized electrodes were measured at various sweep rates and ammonia concentrations with the experimental results given in Figure 6 and Table 1. The lowest of the set of curves in each graph of Figure 6 was recorded in the supporting electrolyte (0.1M KOH) without addition of ammonia. The increase of the current peak value was observed with increasing ammonia concentration and potential sweep rate. After the importance of increased mass transport to the electrode was established, all the experiments were conducted with a rotating platinized platinum electrode.

Current-potential curves obtained potentiostatically at steady state conditions are shown in Figure 7. Current maxima are observed at potentials of about 0.025 V versus SHE. The maximum current increases with concentration in the same manner as in the potentiodynamic experiments.

Maximum current density as a function of ammonia concentration is shown in Figure 8. Maximum current density was found to increase linearly with the square root of the ammonia concentration. This relationship was established on the basis of purely empirical determinations. Experimental data were fitted to several types of relation including linear relation but square root relation gave the highest degree of correlation. The experimental points taken at higher potential sweep rates were more consistent than those taken at lower rates or at steady state conditions.

Maximum current density is plotted versus the square root of the potential sweep rate (V) in Figure 9. A linear relationship is observed at four different ammonia concentrations. At the condition where $V^{\frac{1}{2}} \rightarrow 0$, the ordinate of the figure gives the value of the steady state current for given concentration.

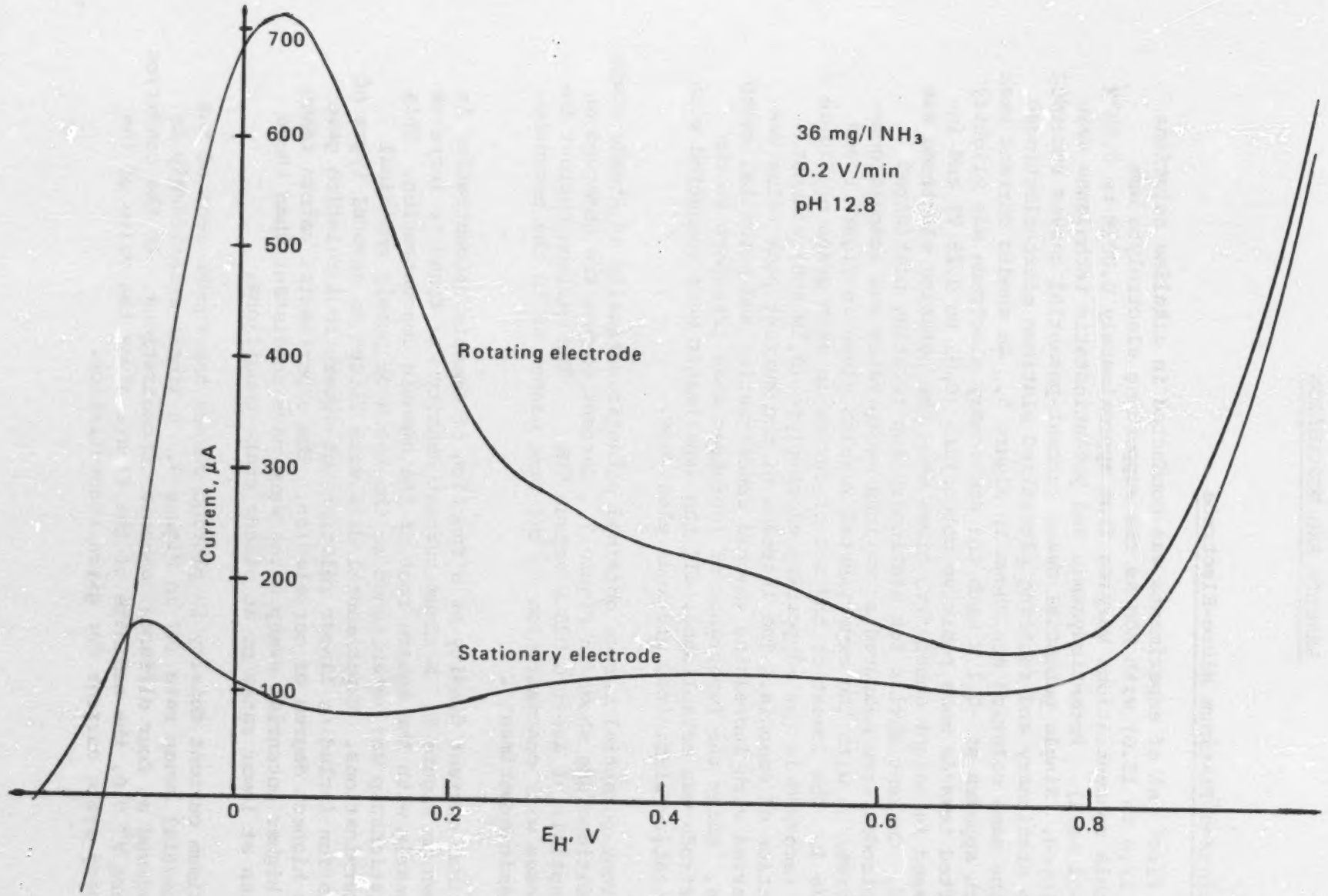


Figure 5. Current Maxima for Rotating and Stationary Electrodes

TABLE 1

Current Maxima for Stationary and Rotating Platinized Platinum Electrode at Various Sweep Rates and Ammonia Concentrations

Sweep Rate [V/min]	Ammonia Conc. [mole/1x10^3]	Maximum Current Density [mA/cm^2] Rotating - i_R	Stationary - i_S	i_R/i_S
0.50	3.0	10.8	2.08	5.19
	1.5	6.2	1.23	5.04
	0.75	3.5	0.85	4.12
0.2	3.0	8.1	1.15	7.04
	1.5	4.4	0.72	6.11
	0.75	2.3	0.5	4.60
0.1	3.0	6.9	0.96	7.19
	1.5	3.9	0.58	6.81
	0.75	1.9	0.38	5.43
0.05	3.0	5.4	0.88	6.14
	1.5	2.7	0.46	5.87
	0.75	1.6	0.29	5.52
steady-state	3.0	3.8	0.67	5.75
	1.5	1.7	0.40	4.25
	0.75	0.96	0.19	5.05

Average $i_R/i_S = 5.61$

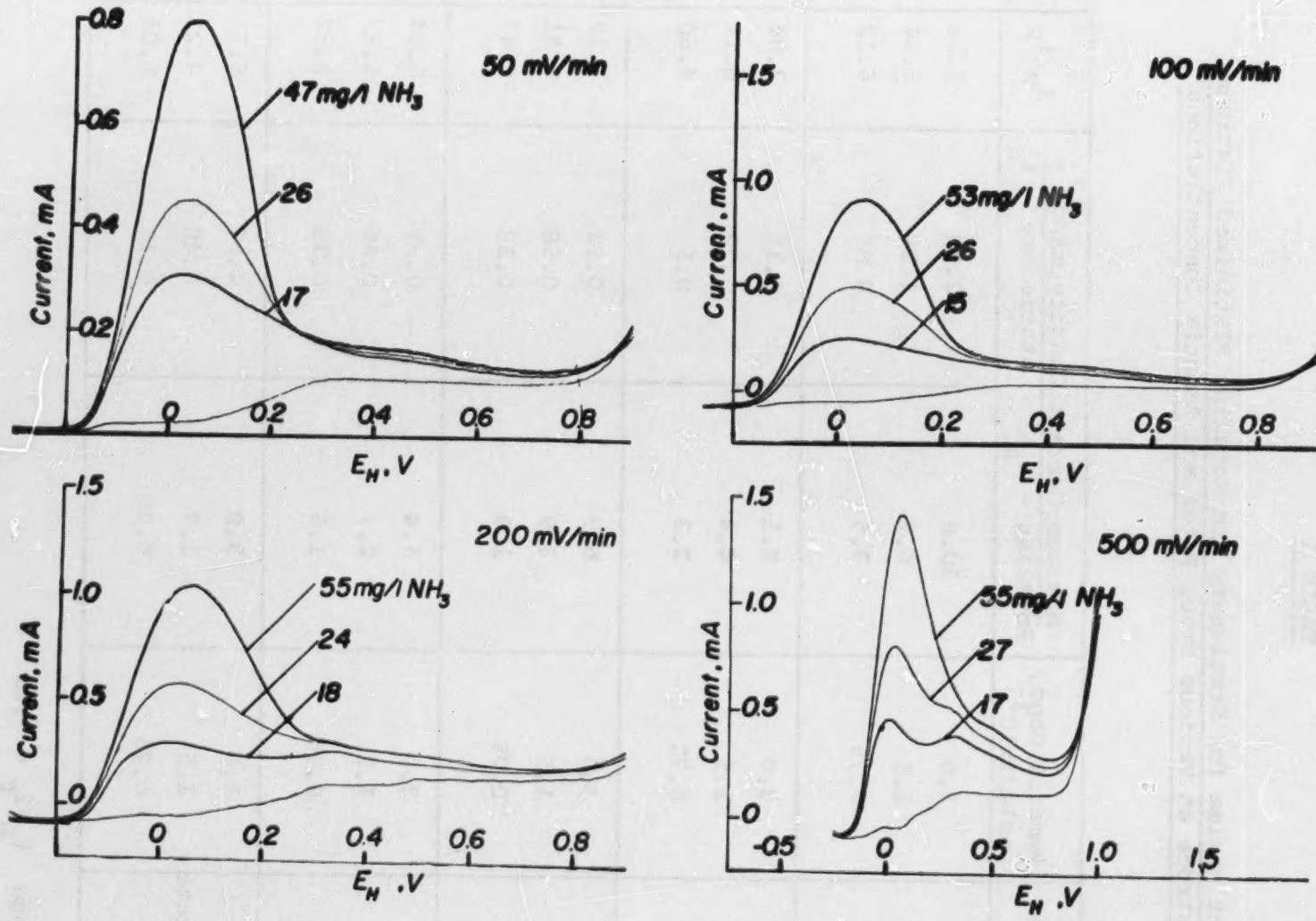


Figure 6. Current Potential Traces for Various Sweep Rates and Ammonia Concentrations

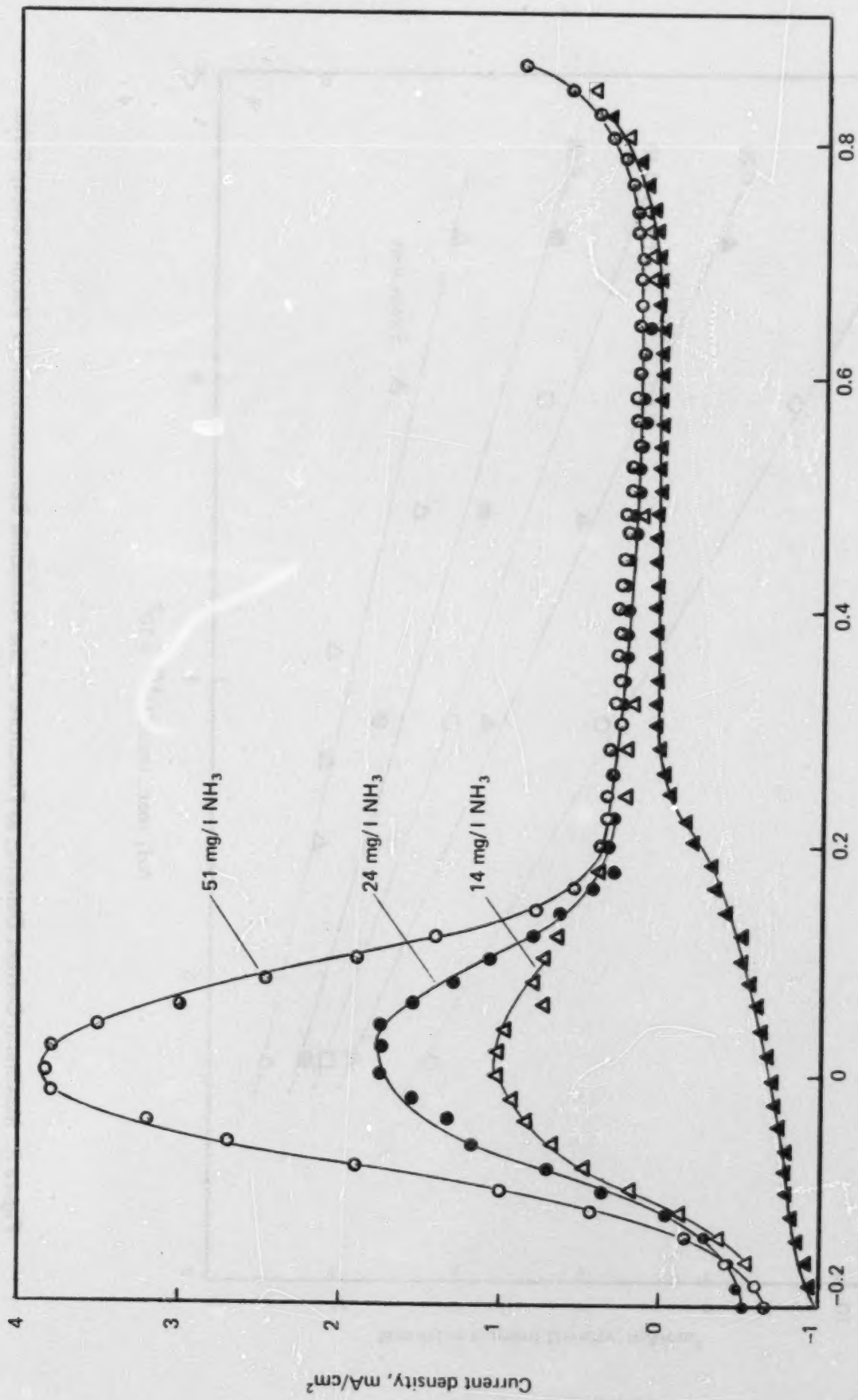


Figure 7. Current Potential Traces for Various Aqueous Ammonia Concentrations from Steady-state Measurements.

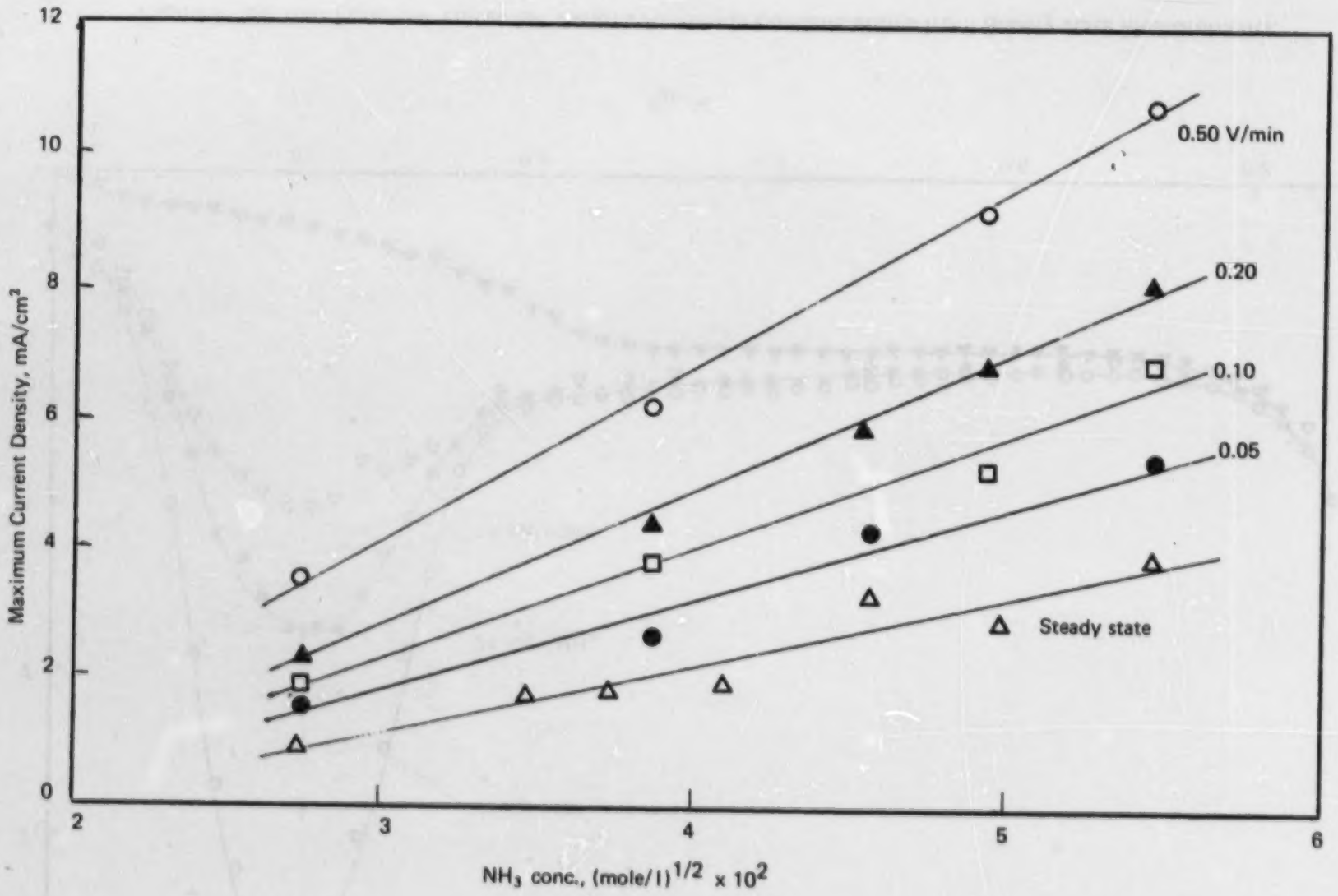


Figure 8. Maximum Current Densities as Functions of the Ammonia Concentration for Various Sweep Rates

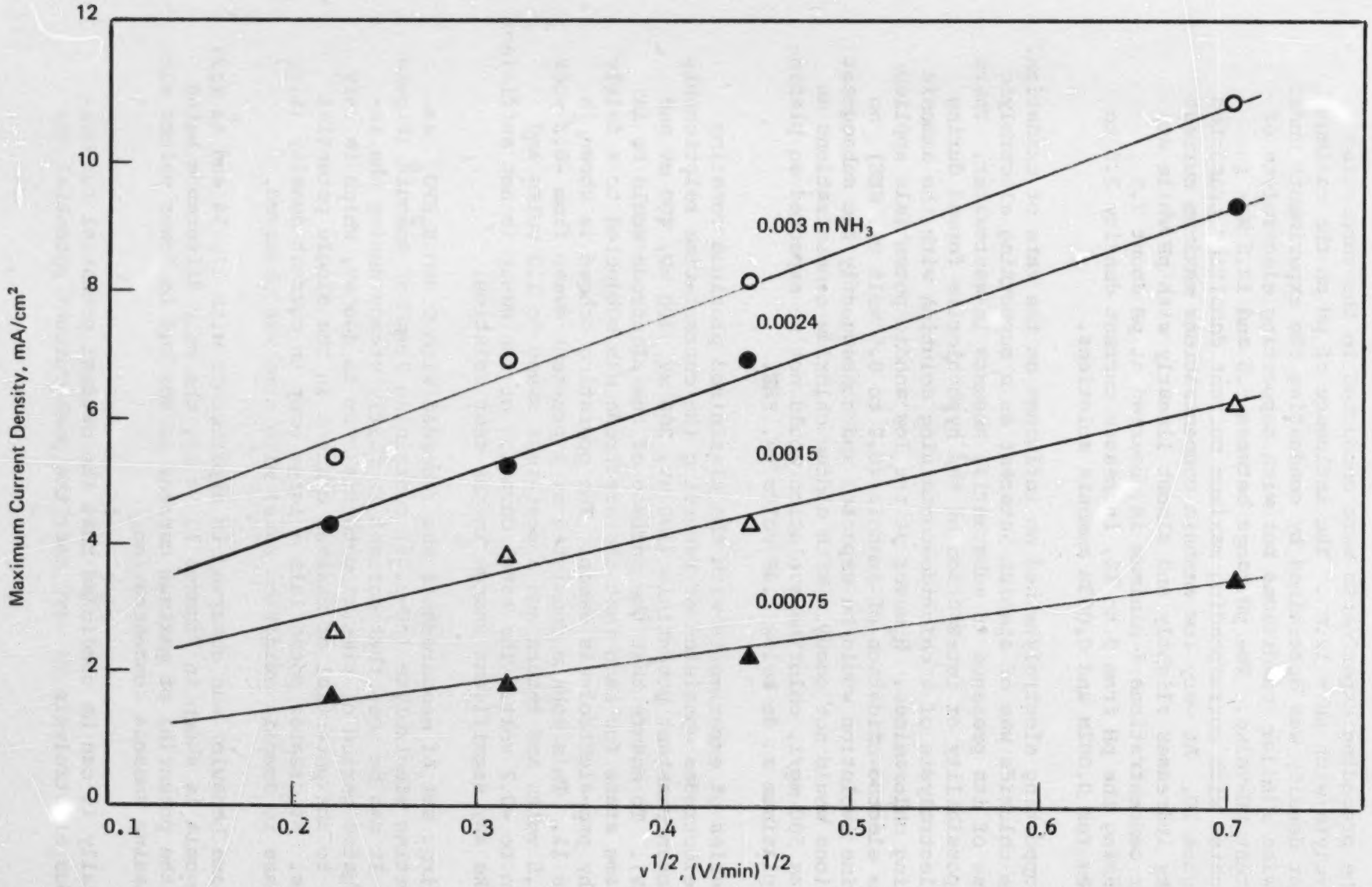


Figure 9. Effect of the Sweep Rate on the Maximum Current Density

All the preceding experiments were conducted in the supporting electrolyte with pH = 12.8 . The influence of pH on the maximum current density was determined by conducting the experiments under otherwise similar conditions but with supporting electrolyte of different pH-value. The pH range between 5.5 and 12.8 was investigated with corresponding maximum current densities presented in Figure 10. At very low ammonia concentrations maximum current density increases slightly and almost linearly with pH while at higher concentrations a minimum is observed at pH about 7.5 . Increasing the pH from 9 to 12, increases current density 2.5 to 3 times for 0.002M and 0.003M ammonia solutions.

The supporting electrolyte had no influence on the rate of oxidation. Sodium chloride was of special interest as a supporting electrolyte because of its presence in substantial amounts in wastewater. There is a possibility of interaction of the hypochlorite formed during the electrolysis of a chloride-containing solution with the ammonia yielding chloramines. However at the low anodic potentials applied in the electro-oxidation of ammonia (0.2 to 0.5 volt vs. SHE) no chlorine evolution would be expected and consequently the subsequent reactions would not occur. With sodium chloride concentrations as high as 500 mg/l, chlorine evolution would not be expected on platinized platinum anode below 1.48 volts vs. SHE.

One series of experiments with the platinized platinum rotating microelectrodes consisted of recording the current-time relationship at chosen constant potentials (100 mV, 200 mV, 300 mV, 400 mV and 500 mV). To ensure that the surface of the electrode would be in the same state for each test the electrode was subjected to a fairly lengthy pre-electrolysis sweep. The operating scheme is shown in Figure 11. This scheme consisted of a pre-test sweep from -0.2 volt to +1.5 volts and return and a post-test sweep to 1.5 volts and return to -0.2 volt. The total duration of the sweep is not sufficient to make any significant change in the test solution.

The first set of measurements was recorded with 0.05M K_2HPO_4 as supporting electrolyte (pH=9.05) containing 7 mg/l of ammonia (Figure 12). It can be seen that current is fairly steady during the investigated period of time at potentials up to 400 mV, which is very close to the potential of maximum current in the single potential sweeps. At greater potentials a large drop in current density (i.e. decrease in ammonia oxidation rate) with time was observed.

The same behavior was observed in experiments with 17, 34 and 51 mg/l of ammonia as shown in Figures 13 to 15, the only difference being that the potential of maximum current is shifted to lower values with increasing ammonia concentration.

Generally it can be concluded that the optimal potential for continuous electrolysis is very near the peak current potential de-

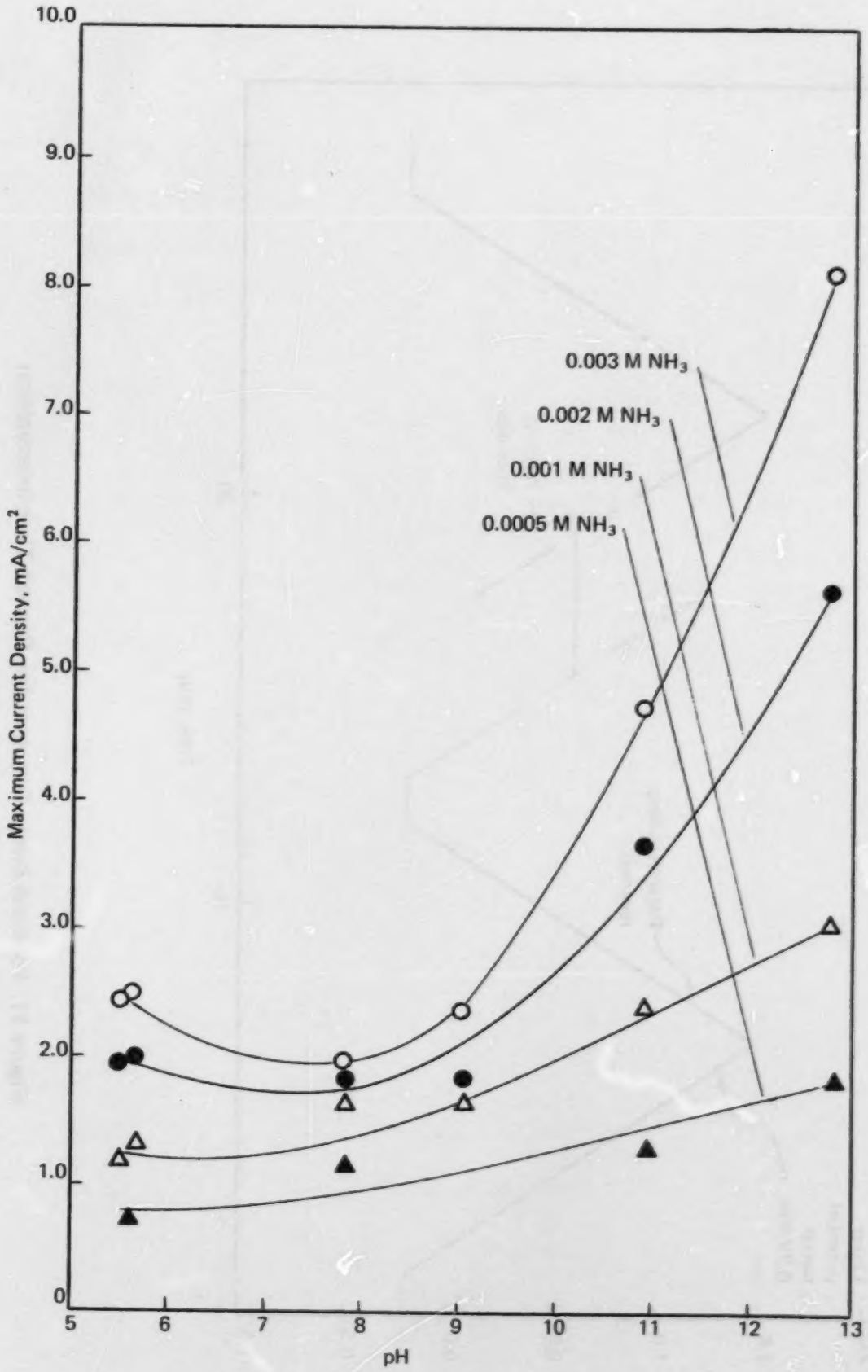


Figure 10. Effect of pH on the Maximum Current Density at Sweep Rate of 0.2 V/min.

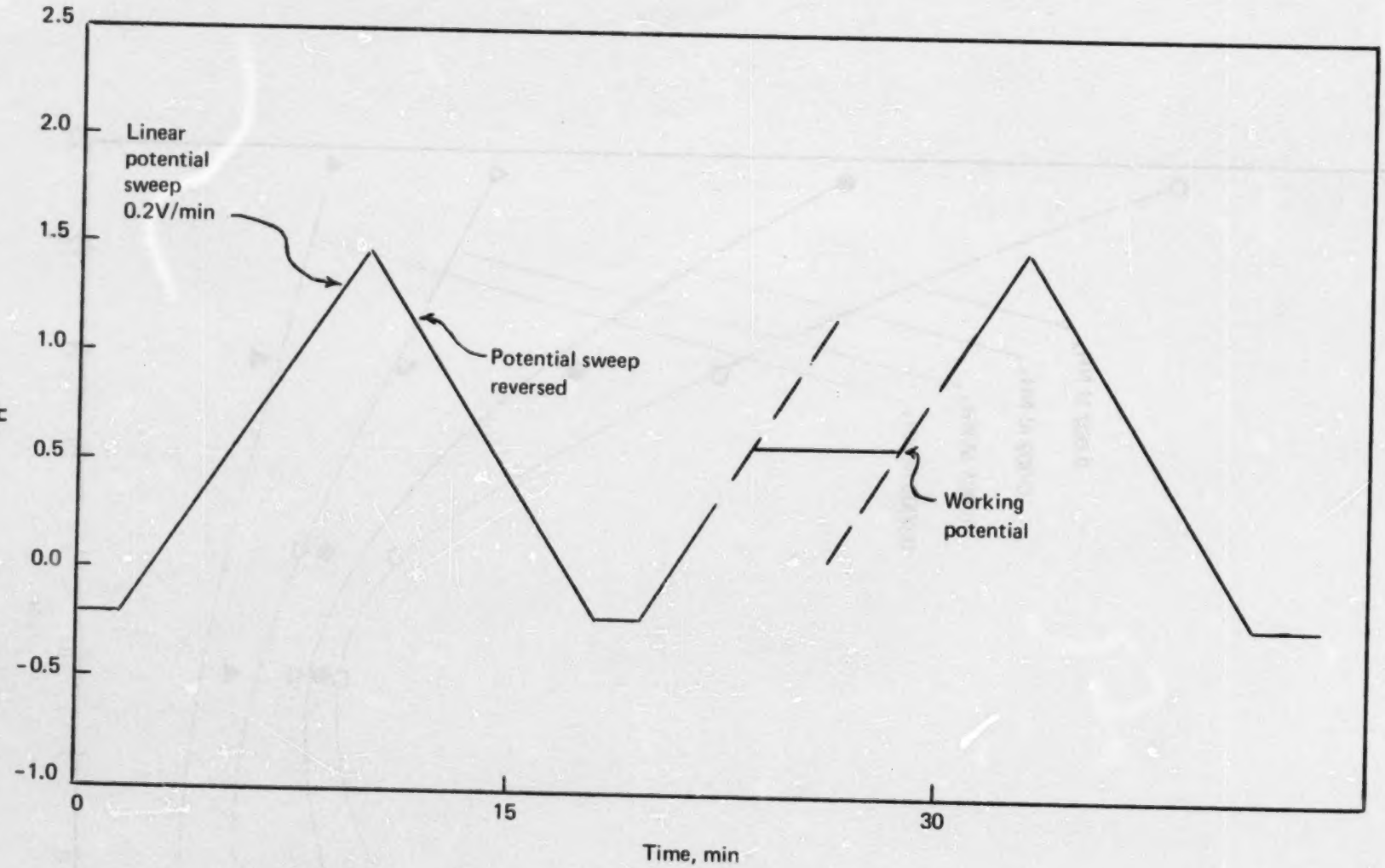


Figure 11. Potential Sweep Sequence for Current-Time Investigation

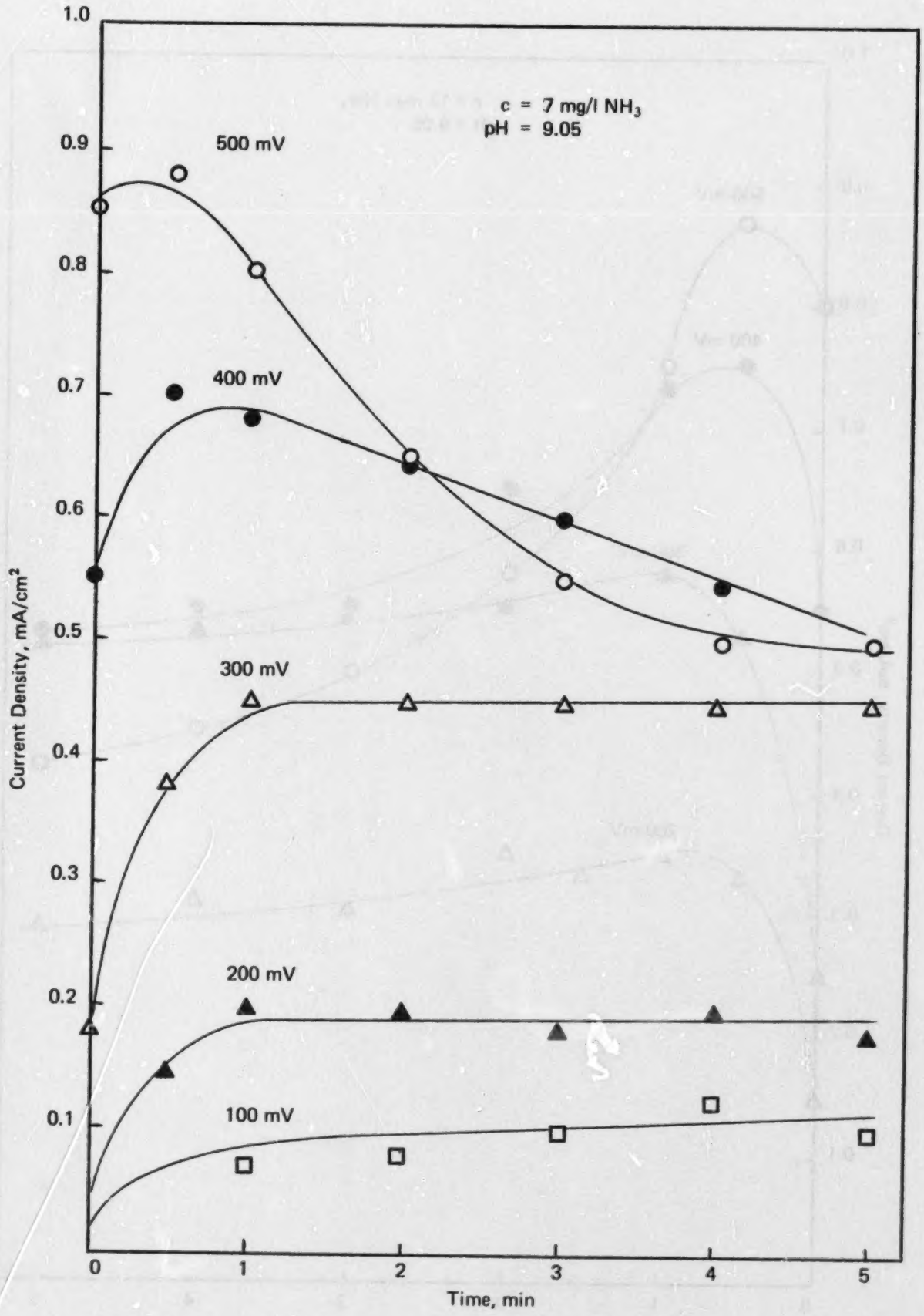


Figure 12. Current-Time Relationship at Constant Potential

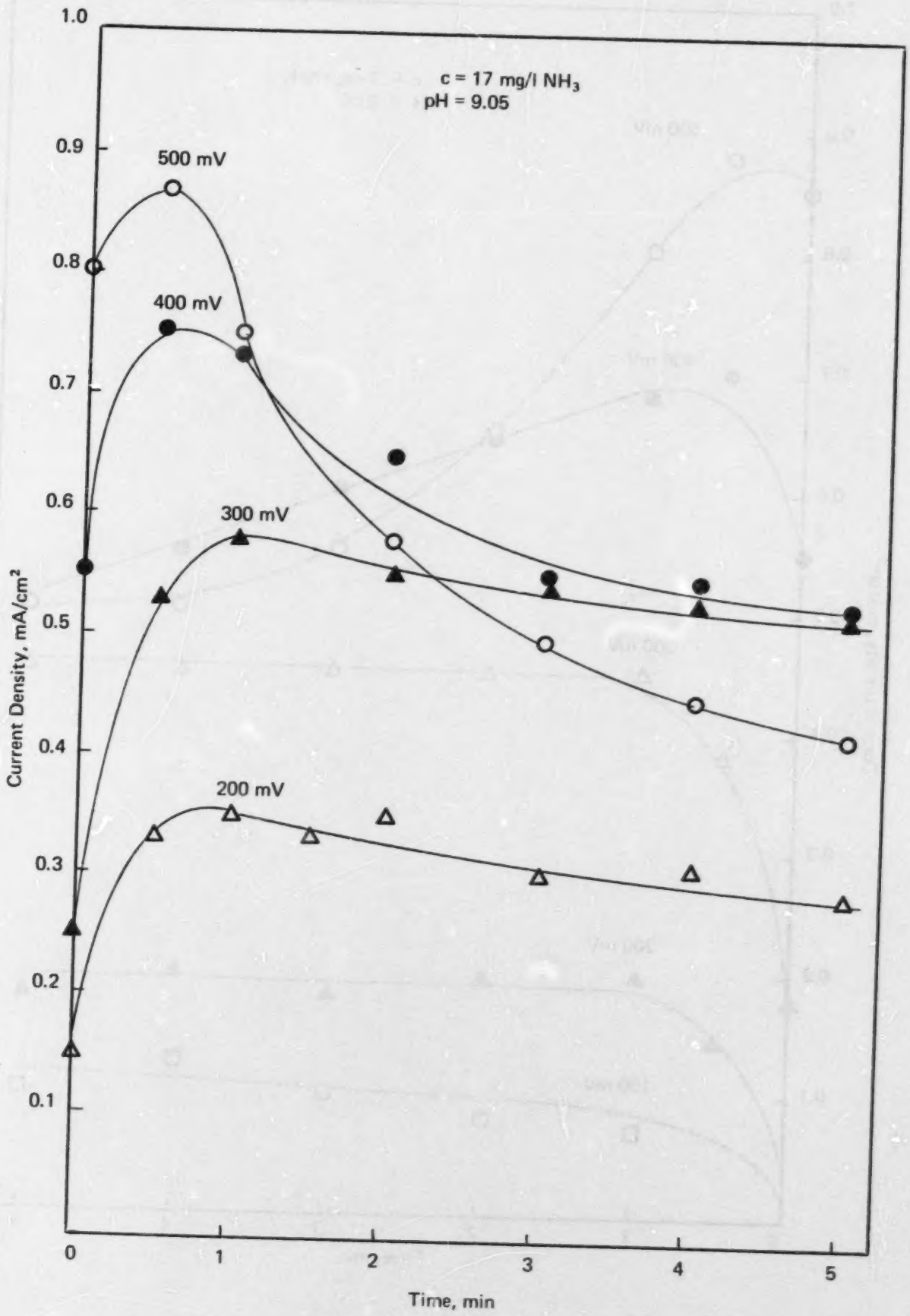


Figure 13. Current Time Relationship at Constant Potential

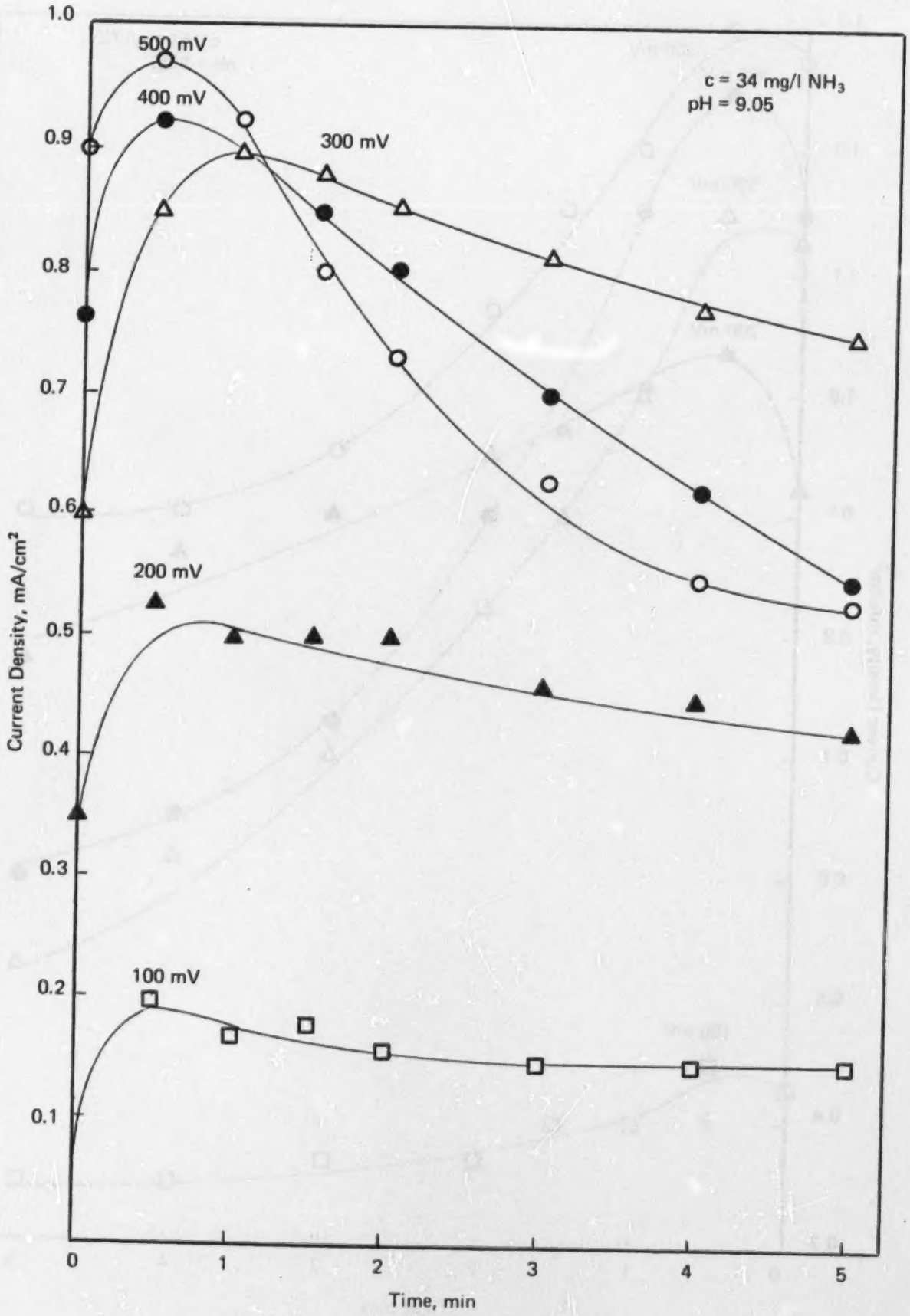


Figure 14. Current Time Relationship at Constant Potential

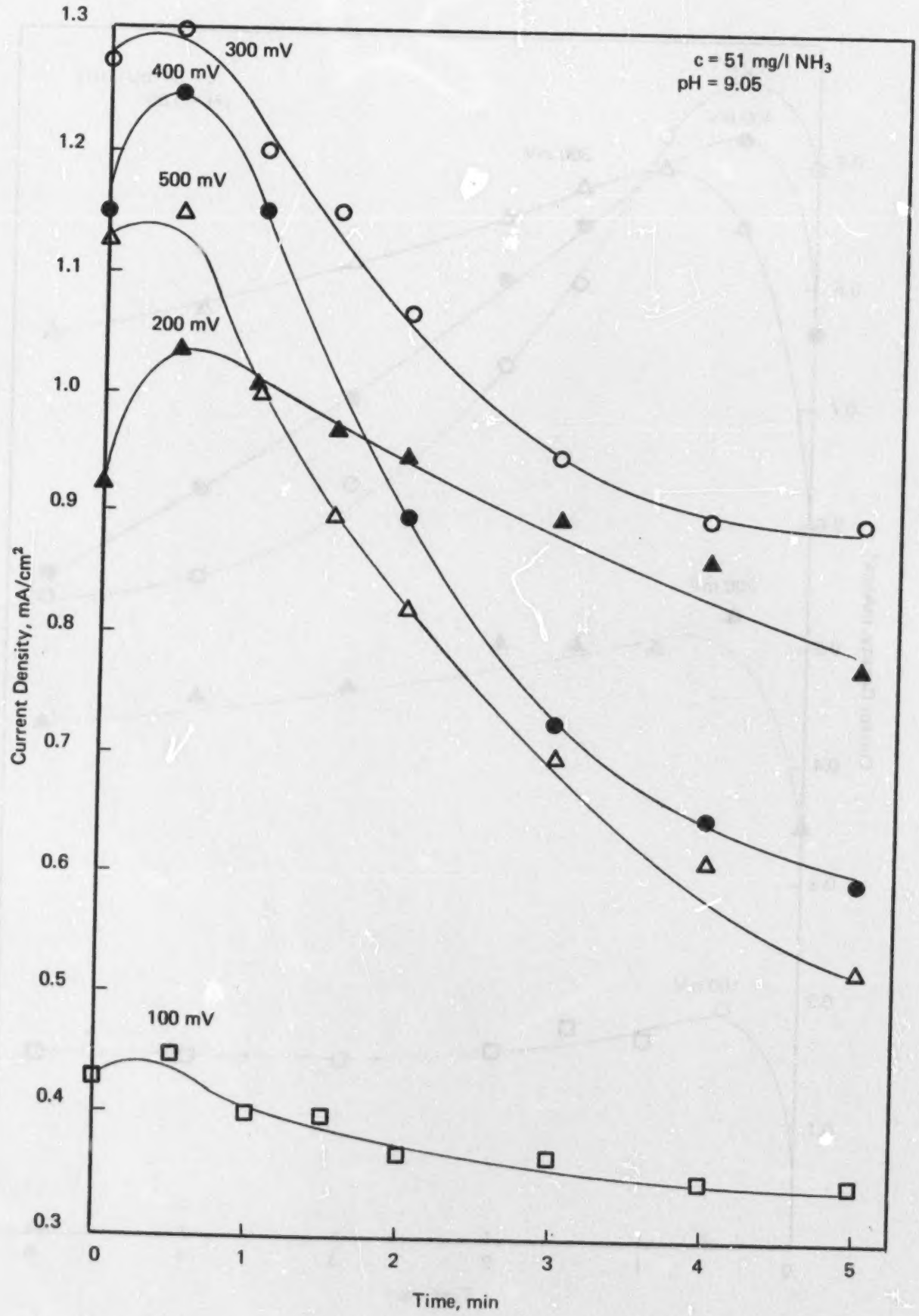


Figure 15. Current-Time Relationship at Constant Potential

termined from single potential sweeps at the given pH and ammonia concentration.

Platinized Platinum Macro-electrode

The degree of completion of the oxidation reaction, current efficiency and reaction products were determined using the larger electrolytic cell (Figure 2) with rotating platinized platinum anode of 20-cm^2 geometric surface area. Test of nitrites, nitrates, hydrazine and hydroxylamine using colorimetric methods were negative. Quantitative analysis of evolved nitrogen as the only gaseous product of the electro-oxidation of ammonia was successfully performed using gas chromatography. Known amounts of the head gas from a sealed cell were used to obtain peaks on the chromatograms (Figure 16b, c, d) which were compared with reference peaks obtained from dilutions of air in helium (Figure 16a). Even with the greatest precautions, traces of air could be detected on the chromatograms, probably due to leakage into the gas-tight syringe. To avoid any mistake about the origin of the detected nitrogen, chromatographic peaks from the test gas were always compared with reference peaks obtained with the air-helium system. Results of the analysis from one experiment are shown in Table 2, and Figure 16. The "observed" value of nitrogen evolved refers to the value obtained by gas chromatographic analysis and the "calculated" value is obtained from the ammonia loss from the solution during the reaction assuming stoichiometric conversion of ammonia to nitrogen.

TABLE 2

Charge [Coulombs]	Volume of N_2 evolved [ml]		Deviation from mean
	Observed	Calculated	
123	3.5	4.9	±16.7%
204	11.1	12.0	± 3.9%
2603	30.2	24.0	±11.4%
2811	33.7	28.5	± 8.3%

Good agreement between the observed and calculated values was noted except at the very beginning of the reaction where amounts of the evolved nitrogen are very small and chromatographic analysis could fail to give accurate results. This agreement, coupled with the absence of other reaction products, indicates a high degree of conversion of ammonia nitrogen to the elemental form. Current efficiency for the oxidation reaction (with assumption of three electron exchange) varied between 50 and 80% depending upon the experimental conditions.

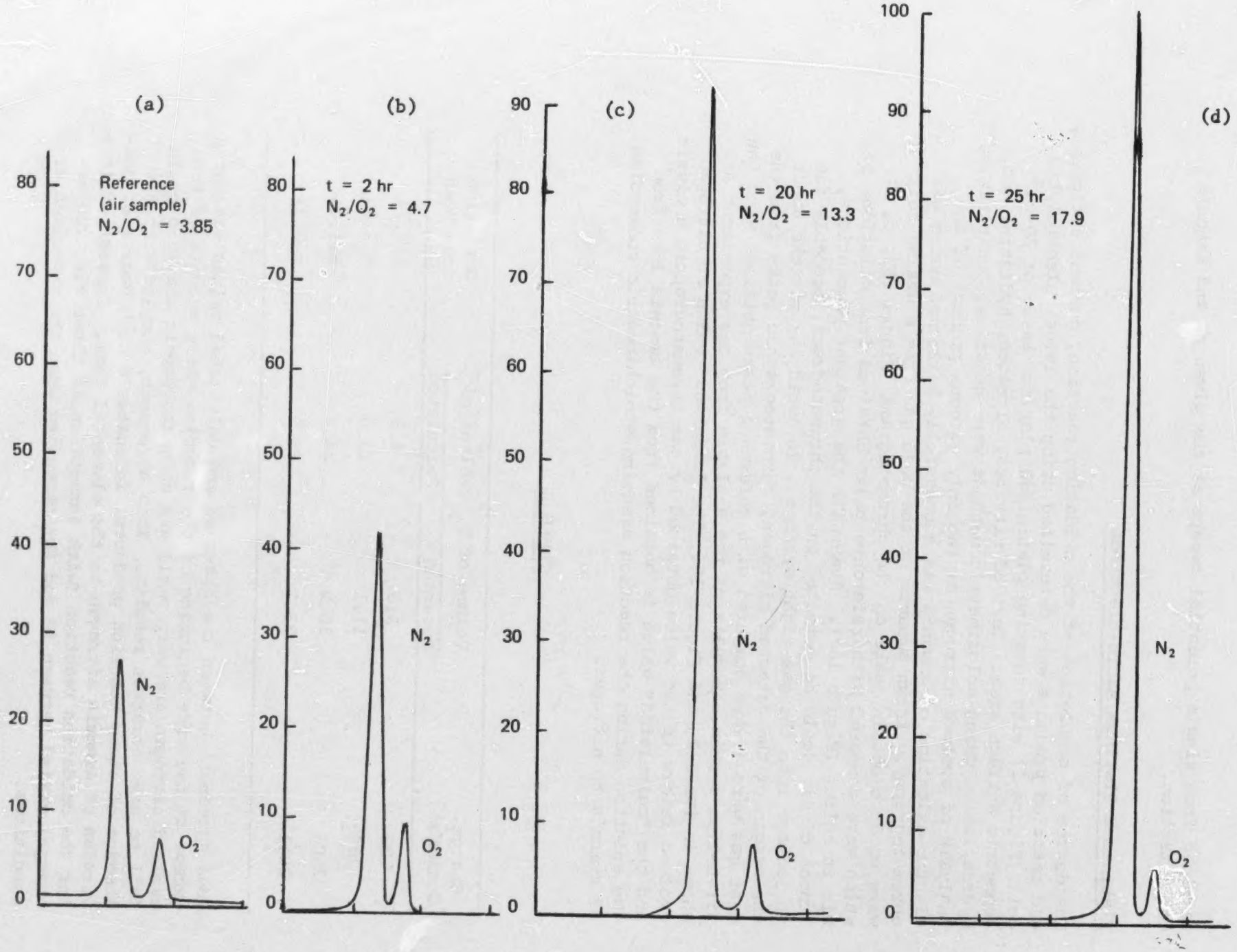


Figure 16. Chromatographic Analysis of Gas Samples Taken at Different Reaction Times

Evaluation of Other Electrocatalysts

Part of the work on electro-oxidation of ammonia consisted of an investigation of a number of different materials as possible electrocatalysts for the ammonia oxidation reaction. The main emphasis was on investigation of noble metals but many non-precious metals, metal oxides, rare earth oxides and commercial proprietary catalysts were evaluated experimentally. Numerous metals showed very high ionic currents at low anodic potentials in phosphate buffer solution and at pH of 8 (e.g. vanadium, rhenium, molybdenum, tungsten, lead, tin). Dissolution of the metallic electrode occurred, followed in a few cases by passivation due to oxide layer formation at high anodic potentials. In some cases a second dissolution region appeared (corresponding to a higher oxidation state of the metal) until finally the oxygen evolution region was achieved. Consequently, the behavior of the electrode surface in the supporting electrolyte and in the anodic potential region which is of interest made investigation of these electrode materials as ammonia oxidation electrocatalysts impossible. All other tested materials are reported in following subsections.

Titanium, Tantalum, Zirconium and Niobium

The metals classified in this group showed complete passivity in the entire investigated anodic potential region due to instant formation of an oxide film. The only current observed was the "leakage current" in the oxygen evolution region. Metal surfaces in this state did not show any catalytic activity for the investigated oxidation reaction.

Proprietary Catalysts

Proprietary metal oxide catalysts developed by Esso Research and Engineering Company for electro-oxidation of hydrazine and for oxidation of propylene and isobutylene were tested for use in the ammonia oxidation process with the results given in Table 3.

Samples designated with catalytic ability of A gave observable oxidation currents; samples designated B gave a barely detectable oxidation rate; and samples designated C showed no oxidation current under the experimental conditions indicated.

On the basis of data given in Table 3 it was concluded that the proprietary oxide catalysts tested have little practical value for ammonia electro-oxidation, since the highest oxidation rate obtained (20 $\mu A/cm^2$ with catalyst 377-87-1) is too low to be feasible in practical unit operation.

TABLE 3

Catalytic Properties of Metal Oxide Catalysts

Catalyst	Catalytic ability	pH	Maximum current density [$\mu A/cm^2$]	General Observations
377-87-1	A	8.15	20	Notes 1 and 2
377-87-2	B	6.55	6	Note 2
377-87-3	C	6.55	0	Note 3
377-87-4	C	6.55	0	Notes 1 and 2
377-87-5	A	6.63	16	
377-87-6	B	6.63	3	
377-87-7A	B	6.63	7	
377-87-7B	C	6.60	0	Notes 1 and 4
377-87-8	C	6.60	0	Notes 1 and 4
377-87-9	C	8.15	0	Note 2
377-87-10	B	6.60	8	
377-87-11	A	8.15	10	
377-87-12	B	8.15	6	

Note 1: High background current
Note 2: Unstable in base
Note 3: Unstable at given pH
Note 4: Poor reproducibility

Proprietary DuPont fuel cell catalysts with semi-conducting properties and with non-precious metal base were recommended by the supplier for testing in the ammonia electro-oxidation process. Electrode samples designated IA-1 to IA-4 by the supplier were tested as well as some of electrodes prepared in our laboratory from powder catalyst designated Mo-0-5 AC-5, but no indication of catalytic properties was found for the ammonia oxidation process.

Rare Earth Oxides

Gadolinium, cerium, neodymium, terbium and thulium oxides were tested anodically using rotating electrodes prepared according to the procedure described in the experimental part of the report. Rare earth oxides were admixed with graphite in the ratio 15:1 and coated on titanium substrates. Potentiodynamic tests in solutions containing 110 mg/l of ammonia at pH of 7.95 to 8.0 gave no indication of electro-catalytic activity for any of the tested materials.

Non-Precious Electro-Deposited Metals and Oxides

A nickel catalyst when prepared in the form of a very finely divided black deposit has been found to be a very good catalyst for some other oxidation reactions. Tests were performed using nickel black as the anode in electro-oxidation of ammonia but no catalytic activity was observed. The same result was found with a smooth nickel anode.

Manganese dioxide electrodeposited on a porous substrate has been successfully used as a fuel cell electrode. The possible application as an ammonia oxidation catalyst was tested by electro-deposition of manganese dioxide on titanium wire and an electrode so prepared was submitted as an anode to the usual testing procedure. A dark grey deposit of MnO_2 was formed on the titanium wire subjected to the electrodeposition procedure described earlier, but no oxidation current was observed when the electrode was tested anodically in the ammonia oxidation reaction.

Noble Metals

Bright Noble Metals

Iridium, gold, platinum, palladium and rhodium were tested anodically. A very low residual current was observed in experiments with iridium. Current was higher with rhodium and gold and substantially higher with platinum and palladium with a wide region of electrostability. No catalytic activity was observed. Experiments with smooth platinum were repeated with the solution pH varied from 8 to 12, but no meaningful results were obtained probably because the exchange current of the ammonia reaction on this electrode was low relative to electrolyte impurity currents.

Electrodeposited Noble Metals

Rhodium-plated rhodium, iridium-plated iridium, palladium-plated palladium, platinum-plated tantalum and titanium and platinized graphite were tested as the anodes for electro-oxidation of ammonia.

Electrodeposition of rhodium gave a fairly bright metallic deposit. In use this electrode gave very low background currents and no appreciable ammonia oxidation current. This is typical of behavior of polished metal surfaces previously tested as oxidation electrocatalysts.

Electroplating of iridium is known to be a very difficult procedure with only a few electroplating references available for obtaining iridium black deposits. The procedure by Ovenden gave a dark grey deposit of iridium, which was completely inert in the process of ammonia oxidation.

The freshly electroplated palladium black catalyst showed some activity at an ammonia concentration of 100 mg/l, but no evidence of any activity at lower concentrations.

Reproducibility of the experimental results obtained with platinized graphite electrodes was not good, but resulting oxidation currents were slightly lower than those obtained with platinized platinum catalyst. The general conclusions are in accordance with those observed with platinized platinum. The region of optimal oxidation rate shifts to higher potentials as the concentration of ammonia and pH of the solution decrease. Oxidation rates increase with ammonia concentration under otherwise similar experimental conditions.

Platinization of titanium and tantalum resulted in black deposits. These were coherent on titanium, but were not very coherent on tantalum. On the basis of the oxidation currents obtained and physical appearance and properties of two electrodes it can be concluded that platinized titanium is preferred to platinized tantalum. Greater currents were observed under otherwise similar experimental conditions in runs with platinized titanium (0.3 mA/cm^2 compared with 0.18 mA/cm^2 for tantalum) and the platinum deposit on titanium showed better coherence probably due to more favorable electrode surface conditions obtained prior to platinization.

Oxidation currents obtained with platinized titanium were about one-eighth those obtained with platinized platinum and about one-sixth those which resulted from using platinized graphite as the electrocatalyst at the same experimental conditions.

Commercial Electrodes

Work on the electrocatalyst screening included testing of DSA (dimensionally stable anode) electrodes with heavy coating from Electrode Corporation, Painesville, Ohio. The coating consists primarily of ruthenium oxide and titanium dioxide. Very high background currents (ranging from 200-250 mA/cm^2), but negligible ammonia oxidation rates, were observed in tests when these electrodes were used as anodes.

Two different types of fuel cell electrodes (American Cyanamid Company) with platinum load of 9 and 10 mg/cm^2 on titanium screen backing were tested. Maximum current densities for both cases (130 and 150 $\mu A/cm^2$ in a solution containing 50 mg/l NH_3) were much too low for the effective use of the catalyst. Both low effectiveness and high cost of the electrode are strong reasons against the use for this work.

Noble Metal Blacks

Commercial platinum black, rhodium black, iridium black and palladium black catalysts were tested alone or in admixture with graphite coated on titanium substrate with Teflon T-30 binder. Composition of the tested platinum black electrode was 74% Pt, 7.4% graphite and 18.6% binder with the total amount of noble metal for surface unit averaging 70 mg/cm^2. Maximum currents observed were 0.85 mA/cm^2 for this fairly high platinum loading. Rhodium black and palladium black electrocatalysts gave no observable oxidation current. Commercial iridium black catalyst was tested alone and mixed with platinum black catalyst. Similar catalytic mixtures were prepared by diluting platinum black with rhodium black and palladium black catalysts. Results from potentiodynamic tests, where single noble metal blacks and their mixtures were used as the anodes for the ammonia electro-oxidation, are shown in Table 4.

TABLE 4

Ammonia Oxidation Rates Obtained with Noble Metal Blacks

Catalyst	Maximum Current Density* [μA/cm^2]	Portion of Noble Metal in Mixture [%]	Weight Ratio of the Components***
Rh	0	90.0	-
Pd	0	90.0	-
Ir	17	90.0	-
Ir + G**	0	79.2	12:1
Pt + Ir	750	85.6	2:1
Pt + Ir + G	450	71.5	10:5:2
Pt + Rh + G	175	69.2	10:6:2
Pt + Pd + G	175	67.8	4:23:1
Pt + G	750	74.0	10:1

* Recorded at potential sweep rate of 0.2 V/min

** G = Graphite

*** Binder content varied between 10 and 20%

Iridium black showed very minute oxidation currents at high noble metal surface concentration but negligible currents at surface concentrations at which considerable oxidation rates were observed with platinum catalyst (750 μA/cm^2 at 74% Pt).

Dilution of platinum with iridium resulted in a slight decrease of the oxidation current compared to a value obtained for pure Pt with the same total amount of noble metal per unit surface. The addition of rhodium black and palladium black to platinum black diminished oxidation rates considerably with the same surface concentration of noble metal.

Overall, the results of mixing platinum black with the other noble metals were not favorable. In the best case (dilution with iridium) almost the same catalytic behavior as for pure platinum catalyst was observed. Dilution with iridium does not lower electrode cost. However the promoter effect of iridium (which is not active itself) was a significant discovery and suggested that a search be made for lower-cost promoter-diluents.

Platinum Black Catalyst

A review of the catalysts which oxidize ammonia with any reasonable rate is given in Table 5. On the top of the list is platinized Pt followed by platinized graphite with a slightly smaller oxidation rate, then commercial platinum black catalyst with 50% less activity and finally platinized titanium and platinized tantalum. As seen from Table 5 all previous work revealed platinum as the only material tested thus far, which would sustain a significant current density.

TABLE 5

Comparison of Ammonia Oxidation Catalysts

Catalyst	Maximum Current Density* [mA/cm^2]	pH	Ammonia Concentration [mg/l]
Platinized Pt	2.3	7.80	100
Platinized graphite	1.65	7.85	51
Platinum black (74% Pt)	0.75	8.10	100
Platinized Ti	0.3	8.15	100
Platinized Ta	0.18	8.15	100

* Recorded at potential sweep rate of 0.2 V/min.

For the process to be economically feasible the catalyst cost should not exceed $5 to $6 per square foot of electrode. This demand requires even distribution and reasonably complete utilization of the electrocatalyst. Since cost limitations necessitate a very small quantity of active material, feasibility would be aided enorm-

ously by the existence of a diluent which would not adversely affect the properties of the material being diluted.

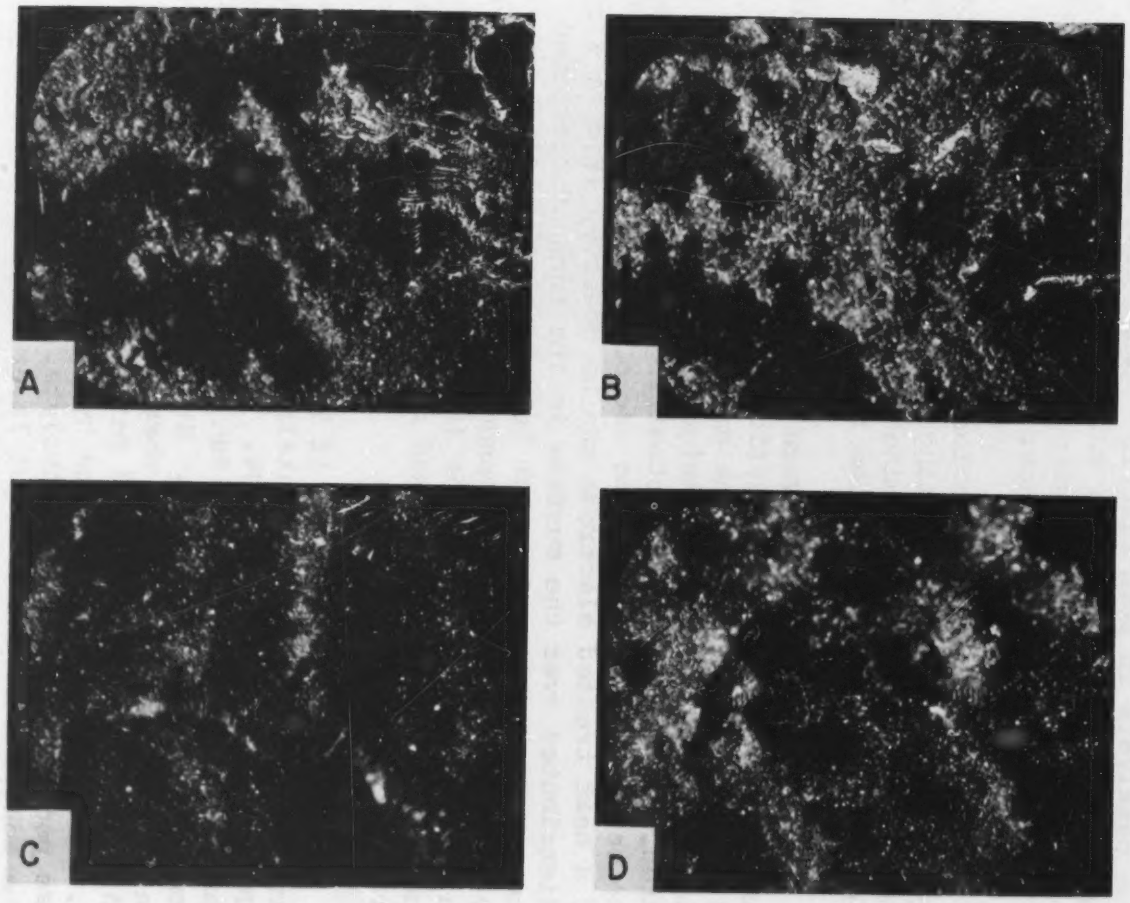
Graphite, generally used for this purpose, and tungsten bronzes, to which was attributed the property of promoter-diluent for platinum catalysts in some electro-organic reactions, were used as diluents in further experimental work. The main emphasis of the continuing work was placed on the preparation of high performance electrodes with low platinum loadings.

In the electrode preparation technique, attempts were made to deposit the catalyst for optimizing the electrochemical characteristics of the electrode. This requires depositing all or most of the catalyst in optimum location, i.e. on the exposed surface.

A series of electrodes were prepared and tested anodically in an attempt to optimize the catalytic and adhesive properties of the coated layer and to minimize the amount of platinum per unit area of electrode surface. Coating techniques #1 and #2 (see Page 11) were compared. On the basis of photomicrographs (Figure 17) there appeared to be difficulties with the use of method #1. Cracks on the surface of a heat treated electrode can be observed (Figure 17c) with platinum distributed over the surface in the form of scattered agglomerates (Figure 17d). Somewhat better platinum distribution and apparently closer adhesion to the tungsten bronze sublayer can be noticed on the hot pressed electrode (Figures 17a, b, and 18). As a result, coating technique #2 was used for the electrode preparation in further work.

To determine the effect of Teflon content, oxidation rates were determined with electrodes containing equal amounts of platinum but with Teflon content of 20 to 50%. The maximum currents from these experiments are plotted as a function of Teflon content and ammonia concentration in Figure 19. Independent of the ammonia concentration the best performance is observed with a Teflon content between 25 and 30%. With increased Teflon content oxidation rates decreased. This is explained by the hydrophobic properties of Teflon, which cause poor contact with electrolyte. With increasing Teflon content the adhesion of the catalyst layer was increased as expected, but this made a poorer electrode on account of the lower oxidation rates. The region of Teflon content below 20% was not investigated because of poor adhesion to the electrodes. Giner, et al (11) have succeeded in the preparation of electrodes with Teflon content in the region of 10 to 20% Teflon. They obtained relatively symmetrical curves of current vs. Teflon content with low currents at low Teflon content.

Specific activity of the catalyst for the electro-oxidation of ammonia was investigated as a function of platinum loading using tungsten bronze and graphite-containing electrodes with a platinum



NOT REPRODUCIBLE

Figure 17. Comparison of the surfaces of hot pressed (a and b) and heat treated electrodes (c and d) each containing tungsten bronze and 1.0 mg Pt/cm^2. M 100X

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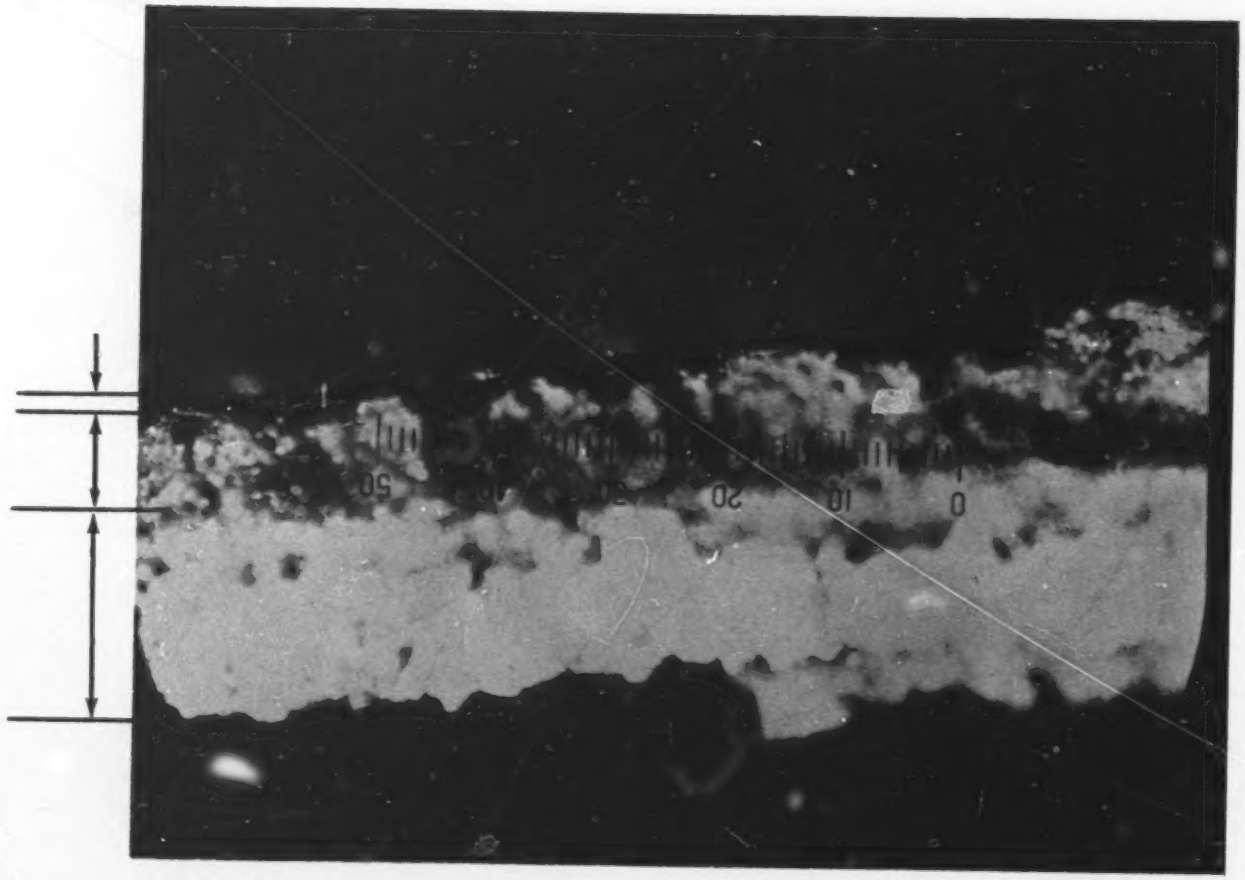


Figure 18. Photomicrograph of a cross-section of a hot pressed electrode containing 1.0 mg Pt/cm². M 50 X

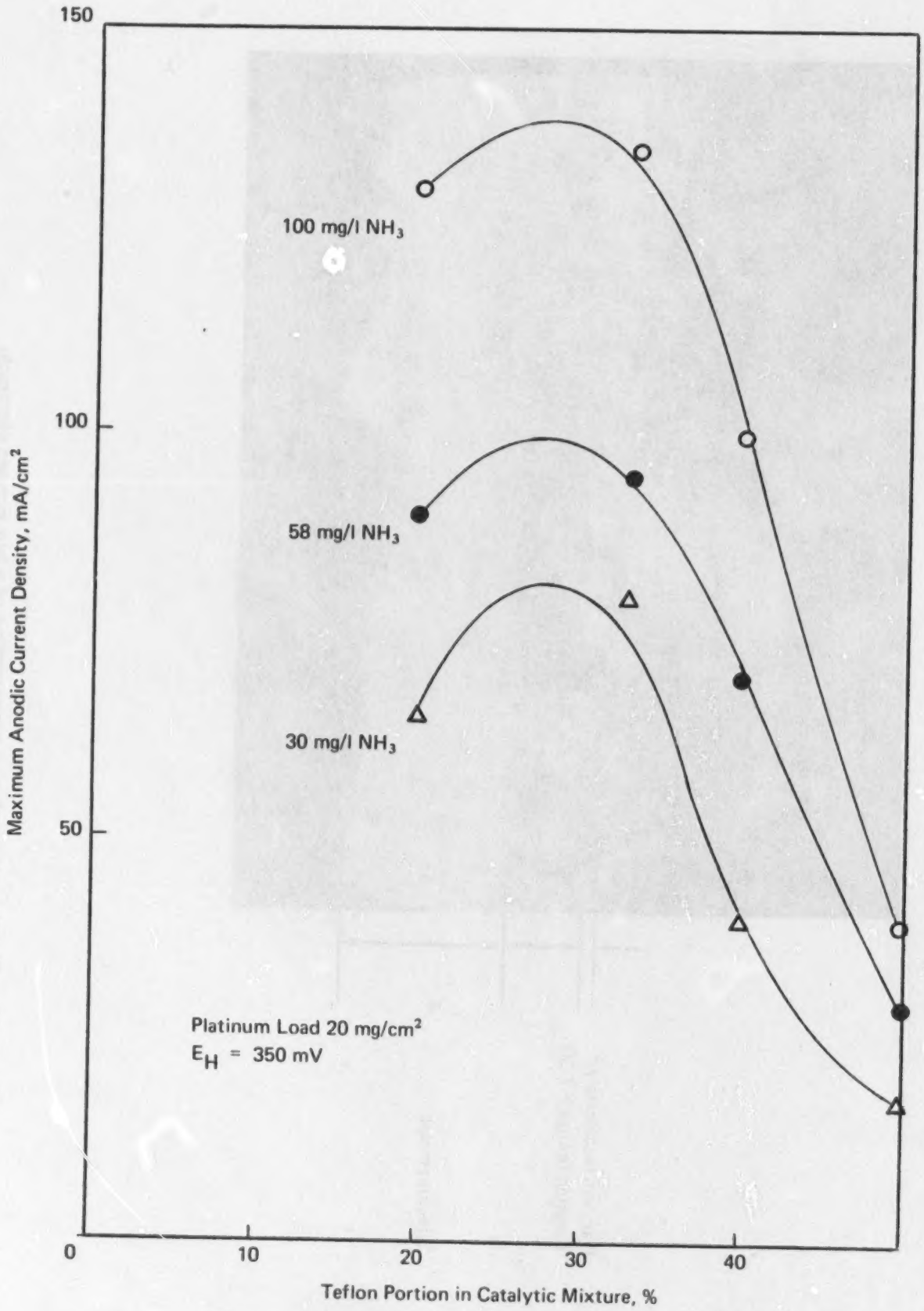


Figure 19. Effect of Teflon Content on Performance of Electrode

load between 0.5 and 20 mg/cm^2. With tungsten bronzes electrode performance was erratic and non-reproducible (Table 6). As a result the correlation between platinum loading and specific activity was poor. It was not possible to determine whether there was any advantage to lower catalyst loadings. With graphite the results were quite reproducible. Data for one ammonia concentration are shown in Table 7. The improvement in specific activity with decreased platinum loading was very clear. A six-fold increase in specific activity was observed between 20 mg/cm^2 and 0.5 mg/cm^2. At the 0.5 mg/cm^2 loading the specific activity with graphite was three times as great as with tungsten bronzes. This comparison is shown in Table 8.

TABLE 6

Specific Activity of Tungsten Bronze-Containing Electrodes with Various Platinum Loadings

Sweep Rate = 0.2 V/min pH = 7.8 ±0.1

Platinum Loading [mg/cm2]	Ammonia Conc. [mg/l]	Specific Activity [μA/mg Pt]
0.5	30	11.0
	58	21.0
	100	40.0
1.0	28	12.0
	56	16.0
	110	22.0
4.0	30	5.0
	60	5.0
	115	6.3
10.0	26	10.0
	52	17.5
15.0	30	19.0
	61	21.7
	121	28.3
20.0	30	10.7
	61	12.7
	121	17.5

TABLE 7

Specific Activity of the Electrocatalyst as a Function of Platinum Loading

SR = 0.2 V/min	pH = 7.8 ±0.1	C = 121 mg/l NH_3
Platinum Loading [mg/cm^2]	Peak Current [$\mu A/cm^2$]	Specific Activity [$\mu A/mg$ Pt]
0.5	56	112
1.0	139	139
2.0	114	58
3.0	120	40
4.0	124	31
5.0	150	30
6.0	174	29
7.0	175	25
8.0	240	30
9.0	270	30
10.0	200	20
15.0	328	22
20.0	360	18

TABLE 8

Comparison Between the Performance of Tungsten Bronze and Graphite Containing Electrodes with 0.5 mg Pt/cm^2

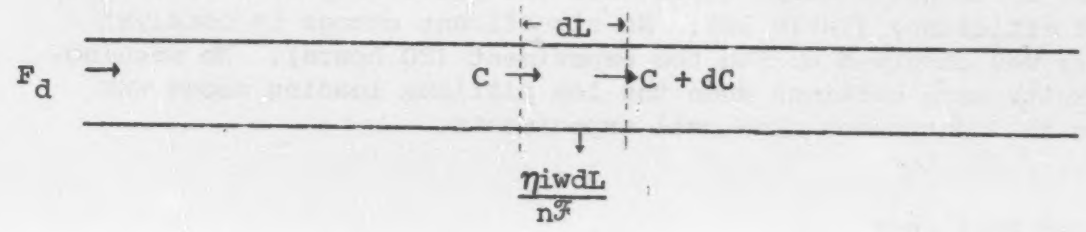
Sweep Rate = 0.2 V/min pH = 7.8 ±0.1

Ammonia Conc. [mg/l]	Specific Activity [$\mu A/mg$ Pt]	
	Tungsten Bronze	Graphite
30	11	50
60	21	78
120	40	112

Continuous Flow Apparatus

Cell Design

The design equation was derived from a material balance around a differential length of flow path. In this derivation, F_d is flow rate in ml/sec, C is local concentration in moles/liter, i is current density in mA/cm^2 and η is current efficiency. L is total flow path length and dL is differential flow path length both in cm, w is path width in cm. $\mathcal{F}$ is 96,500 A-sec/eq and n is 3 eq/mole.



$$F_d C = F_d(C + dC) + \frac{\eta iwdL}{n\mathcal{F}} \qquad [8]$$

$$-F_d dC = \frac{\eta iwdL}{n\mathcal{F}} \quad \text{or} \quad -\frac{dC}{i} = \frac{\eta wdL}{F_d n\mathcal{F}} \qquad [9]$$

If, as a first approximation, the current density is assumed to be constant along the flow path, equation [9] can be directly integrated to give:

$$F_d(C_{in} - C_{out}) = \frac{\eta i_{avg} wL}{n\mathcal{F}} \qquad [10]$$

This approximation was used in setting up the experimental cell. For greater accuracy i should be expressed as a function of C. This refinement was not considered necessary for the present study.

Cell Operation

The results from four typical experiments employing electroplated platinum catalysts are presented in Table 9. Feed concentrations, volumetric feed rates and spacer thickness were varied from experiment to experiment. Ammonia conversion increased with increased current density up to a limiting value of about 0.4 mA/cm^2, when it started decreasing as the corresponding potential suddenly rose to the value

where oxygen evolution starts. An optimum anodic potential is found to be in agreement with previous determinations (micro-tests), i.e. between 350 and 550 mV vs. SHE. With the exception of a relatively high current efficiency at very low current density (η = 0.402 at 0.158 mA/cm^2), the current efficiency varied between 12.8 and 28.2% and averaged 20.9%.

Commercial powdered platinum catalyst was tested in the continuous flow cell at two different platinum loadings, about 50 mg Pt/cm^2 and 1 mg Pt/cm^2. The experiment with the high platinum loading was carried out at two different current densities, 0.238 and 0.397 mA/cm^2, yielding 23 to 40% ammonia conversion and proceeding with 23 to 30% current efficiency (Table 10). No significant change in catalyst activity was observed during the experiment (20 hours). No meaningful results were obtained when the low platinum loading anode was used in the continuous flow cell experiments.

Estimated Unit Cost

An estimate was made of process economics for the ammonia oxidation unit using a platinum catalyst. This estimate is based on a plate and frame design similar to Ionics electrodialysis equipment. Since the total currents are low, a back-to-back arrangement with each anode and each cathode serving two cells is contemplated. This should reduce electrode fabrication costs and allow the cathodes to be made of a comparatively inexpensive material such as steel, carbon or graphite.

The energy required for treatment of 1000 gal. of water, P, is given by

$$P = I \cdot t \cdot V$$

$$= \frac{n \cdot \mathcal{F} \cdot \Delta C \cdot 3.785 \cdot V \cdot 10^{-3}}{3600 \cdot MW}$$

$$= 0.018 \cdot \Delta C \cdot V \qquad [11]$$

where P is in KWH/1000 gal., I·t is coulomb load in amp.hrs/gal., V is voltage per cell, ΔC is the decrease in concentration in mg/l, n is 3 eq/mole, $\mathcal{F}$ = 96500 coulomb/eq and MW is 17 gm/mole. The voltage is estimated at 0.6 volt per cell. This assumes an anode potential of +0.4 volt, a cathode potential of -0.1 volt (both with respect to a standard hydrogen electrode) and 0.1 volt for overcoming the path resistance. This would result from a c.d. of 1.5 mA/cm^2, a solution conductivity equivalent to that of 0.01N NaCl and a path length of 0.03 inch. Total voltage is virtually independent of current density.

TABLE 9

Experimental Data from the Continuous Flow Electrolytic Cell with Platinum Electroplated Titanium Anode

$i[mA/cm^2]$	E_H[Volts]	$C_o[mole/l]x10^3$	$\frac{C_i - C_o}{C_i}$	η
$C_i = 1.69x10^{-3}$ mole/l, F_d = 100 ml/hr, V_o = 0.402 cm/sec, t_R = 227 sec				
0.158	0.352-0.392	1.19	0.295	0.402
0.317	0.432-0.457	1.01	0.402	0.273
0.397	0.502-0.527	0.806	0.524	0.282
0.476	0.702	0.923	0.453	0.368
$C_i = 1.6x10^{-3}$ mole/l, F_d = 75 ml/hr, V_o = 0.29 cm/sec, t_R = 300 sec				
0.238	0.422-0.437	1.01	0.37	0.237
0.397	0.442-0.457	0.69	0.57	0.220
$C_i = 1.78x10^{-3}$ mole/l, F_d = 75 ml/hr, V_o = 0.29 cm/sec, t_R = 300 sec				
0.238	0.457-0.502	1.33	0.253	0.125
0.317	0.477-0.522	1.22	0.315	0.165
0.476	0.627-0.682	0.935	0.475	0.170
$C_i = 1.78x10^{-3}$ mole/l, F_d = 70 ml/hr, V_o = 0.54 cm/sec, t_R = 163 sec				
0.238	0.337-0.362	1.25	0.298	0.200
0.317	0.347-0.352	1.15	0.354	0.177
0.476	0.447-0.557	1.06	0.404	0.181

TABLE 10

Experimental Data Obtained with Commercial Platinum Black Catalyst

30 mg Pt/cm^2 $C_i = 1.69x10^{-3}$ mole/l, F_d=110 ml/hr, V_o=0.442 cm/sec t_R=206 sec

$i[mA/cm^2]$	$C_o[mole/l]x10^3$	$\frac{C_i - C_o}{C_i}$	η
0.238	1.29	0.233	0.23
0.397	1.00	0.408	0.30

Using V of 0.6 volt and a power cost of 1¢/KWH, the cost of power for removing 20 mg/l of ammonia would be 0.22¢/1000 gal. at 100% current efficiency. The experimentally determined current efficiency for the process was 25% which results in a cost of 0.9¢/1000 gal.

The electrode surface area required to treat one gallon per hour, A_s is given by:

$$A_s = \frac{0.018 \cdot \Delta C}{i}$$

where A_s is the area in $ft^2/gal \cdot hr^{-1}$ and i is the current density in A/ft^2. An average current density value of 0.05 A/ft^2 was obtained with platinum black-graphite containing electrocatalyst with platinum load of about 0.5 mg/cm^2. Using this value, A = 7.2 $ft^2/gal \cdot hr^{-1}$.

The electrode cost is based on use of 10 mil titanium anodes with a coating of 0.5 mg/cm^2 of platinum. This thickness was considered optimal in the trade-off between material cost and satisfactory physical properties. Titanium sheet in this thickness currently sells for about \$2.00/ft^2 in quantity. Since both sides are used the cost per square foot of usable area is slightly over \$1.00. A platinum coating of 0.5 mg/cm^2 would require \$4 of platinum/ft^2 assuming that gasketed areas were not platinized. Other components and installations are estimated at \$2.00 per square foot of electrode based on installed electrodialysis units. Total installed cost of the unit per square foot of electrode area amounts to \$7.00.

The capitalized cost per 1000 gal., C, using a rate of 7% per annum and 90% load factor, is given by:

$$C = A_s \cdot C_A \cdot 0.89 \cdot 10^{-2}$$

where C_A is the installed cost of the unit in dollars per square foot of electrode. Using 7.2 $ft^2/gal \cdot hr^{-1}$ for A_s and \$7.00 per ft^2 for C_A, C = 44.8¢/1000 gal.

Total of power cost and capital cost for removal of 20 mg/l of ammonia amounts to 0.9 + 44.8 = 45.7¢/1000 gal.

Substantial improvement in catalyst activity would be required before this ammonia removal method could be considered practical. A twenty-fold increase in current density from 0.05 to 1.0 A/ft^2 would be needed to reduce the cost of equipment to a reasonable value of 2.2¢/1000 gal.

Although reductions in electrode cost may be possible, they could not be great enough to make the process practical at the assumed current

density of 0.05 A/ft^2 . Installation of the unit and cost of components other than anodes is estimated at $2.00 per ft^2 of anode. The costs would result in an amortization cost alone of 13¢/1000 gal. This is too high a cost to make electro-oxidation competitive with other ammonia removal methods.

CONCLUSIONS

Technically, electro-oxidation has a number of desirable attributes as a means of removal of ammonia from wastewater. Under conditions of ammonia concentration and pH typical of treatment effluents, the reaction proceeds stoichiometrically to nitrogen with no other oxidation products. Oxidation occurs in concentrations as low as 2 mg/l. For the electrochemical reaction the cost of power would be very low, 1¢/1000 gal or less. The only electrocatalyst on which the reaction was found to proceed with any reasonable rate, however, was platinum. Because of the high price of platinum, the capital investment would be too high for the process to be economically feasible.

To reduce the capital cost, a considerable search was made for other possible electrocatalysts. These included a wide variety of materials including noble metals, metal oxides, commercial electrocatalysts and proprietary catalysts. No material was found which was an improvement over platinum. Some economic advantage resulted from use of extenders like graphite and tungsten bronzes. However, neither of these was sufficiently effective to lower the catalyst cost per unit area to a suitable value.

While the process is not economically feasible at the present time, future work directed toward other processes may result in the development of a cheaper catalyst which would operate at a higher current density. No approaches to more economical electrodes are known at present which would justify additional work.

REFERENCES

1. T. Katan and R. J. Galiotto, J. Electrochem. Soc. 110, 1022 (1963).

2. H. G. Oswin, and M. Salomon, Can. J. Chem. 41, 1968 (1963).

3. A. R. Despić, D. M. Dražić and P. M. Rakin, Electrochim. Acta 11, 997 (1966).

4. D. Sparbier and G. Wolf, Z. Naturforsch, 19a, 614 (1964).

5. E. Müller and F. Spitzer, Z. Elecktrochem, 11, 917 (1905).

6. V.O. Reitlinger, Z. Elektrochem, 20, 268 (1914).

7. D. J. G. Ives and G. J. Janz, Reference Electrodes, Academic Press, New York (1961).

8. P. J. Ovenden, Nature, 179, 39 (1957).

9. L. W. Niedrach and I. B. Weinstock, Electrochem. Technol. 3, 270 (1965).

10. M. E. Straumanis, J. Am. Chem. Soc. 71, 679 (1949).

11. J. Giner, J. M. Parry, S. Smith and M. Turchan, J. Electrochem. Soc. 116, 1692 (1969).

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27 Abstract An objective of the study was to determine the feasibility of electrooxidation of ammonia as a possible new method for ammonia removal during sewage treatment. Initial tests were conducted with platinized platinum and showed that ammonia decomposition occurred in a narrow potential range with high coulombic efficiency, assuming a three-electron exchange per ammonia molecule. Conversion of nitrogen to the elemental form was shown by analysis of the gas from the anode. Analysis of the electrolyzed water for nitrite, nitrate hydrazine and hydroxylamine indicated these materials were not formed in measurable quantities. Their absence suggests a high degree of conversion of ammonia nitrogen to the elemental form.

Following the initial determination of technical feasibility, a survey was made of electrodes having lower cost than platinized platinum. Only electrodes containing a significant amount of platinum were found capable of converting ammonia nitrogen to elemental nitrogen. The cost of these electrodes is too high to make this ammonia removal method competitive with other existing methods. A cheaper electrode that can operate at significantly higher current densities is needed to bring the cost in line with the cost of these other methods. (Brunner - WQO)

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